MEMBRANE DEVELOPMENT AND FABRICATION FOR REVERSE OSMOSIS AND ULTRAFILTRATION

PART 4

Report to the

Water Research Commission

by

N.K.H. Strohwald, E.P. Jacobs and R.D. Sanderson

Institute for Polymer Science
University of Stellenbosch
Stellenbosch
7600

WRC Report No 172

December 1987

CLASSIFIED - NOT AVAILABLE FOR DISTRIBUTION

MEMBRANE DEVELOPMENT AND FABRICATION FOR REVERSE OSMOSIS AND ULTRAFILTRATION

by

NKH STROHWALD, EP JACOBS and RD SANDERSON

FINAL REPORT TO THE
WATER RESEARCH COMMISSION

BY THE
INSTITUTE FOR POLYMER SCIENCE
UNIVERSITY OF STELLENBOSCH

PART 4:
TECHNOLOGY TRANSFER:
THE DEVELOPMENT OF TUBULAR UF TECHNOLOGY FOR INDUSTRIAL USE

WRC PROJECT: 172

MEMBRANE DEVELOPMENT AND FABRICATION FOR REVERSE OSMOSIS AND ULTRAFILTRATION

THIS PROJECT WAS FUNDED BY THE WATER RESEARCH COMMISSION AND CARRIED OUT AT THE INSTITUTE FOR POLYMER SCIENCE AT THE UNIVERSITY OF STELLENBOSCH

THE REPORT IS PRESENTED IN FOUR PARTS:

PART 1: EXECUTIVE SUMMARY TO THE FINAL REPORT
EP JACOBS and RD SANDERSON

PART 2: STATISTICAL AND NUMERICAL TECHNIQUES IN THE OPTIMIZATION OF MEMBRANE FABRICATION VARIABLES
EP JACOBS and RD SANDERSON

PART 3: THE CHEMISTRY OF POLY-2-VINYLIMIDAZOLINE REVERSE OSMOSIS MEMBRANES
MJ HURNDALL and RD SANDERSON

PART 4: TECHNOLOGY TRANSFER:
THE DEVELOPMENT OF TUBULAR UF TECHNOLOGY FOR INDUSTRIAL USE
(CLASSIFIED - NOT AVAILABLE FOR DISTRIBUTION)
NKH STROHWALD, EP JACOBS and RD SANDERSON

ACKNOWLEDGEMENT

The Steering Comittee, co-opted members and referees for this project consisted of the following persons:

Dr CF Schutte	Water Research Commission (Chairman)
Mr JP Barnard	Bakke Industries (Pty) Ltd
Prof CA Buckley	University of Natal
Mr NA Dowler	University of Stellenbosch
Prof W Engelbrecht	University of Stellenbosch
Dr PF Fuls	National Institute for Water Research
Dr OO Hart	Water Research Commission
Mr BA Hendry	Bakke Industries (Pty) Ltd
Dr MJ Hurndall	University of Stellenbosch
Dr EP Jacobs	University of Stellenbosch
Dr S Kuehl	University of Stellenbosch
Mr PE Odendaal	Water Research Commission
Dr C Patterson-Jones	University of Cape Town
Dr HS Pienaar	Universiteit van Stellenbosch
Dr LS Rayner	University of Stellenbosch
Dr RD Sanderson	University of Stellenbosch
Prof DF Schneider	University of Stellenbosch
Mr DB Smit	Bakke Industries (Pty) Ltd
Prof JJ Smit	University of Potchefstroom for CHE
Mr PL Swart	Bakke Industries (Pty) Ltd
Dr AJ van Reenen	University of Stellenbosch
Mr PW Weideman	Water Research Commission (Secretary)

The financing of the project by the Water Research Commission and the contribution by the members of the Steering Committee are acknowledged gratefully.

EXECUTIVE SUMMARY

This study formed part of a programme designed to contribute to the development and establishment of ultrafiltration (UF) technology.

The four goals of this study can be summarized as follows:

i) to establish the technology of laboratory developed membranes for the industrial production of commercially useful tubular ultrafiltration membranes made from poly(ether sulphone).

ii) to develop tubular ultrafiltration modules through modification of RO membrane technology which exists at Membratek.

iii) to evaluate the membranes and modules in bench and pilot studies on real process streams.

iv) to commercialize the technology through the design, construction and commissioning of industrial sized systems.

The work proved the following:
UF membranes which were developed, showed good integrity and quality when compared to commercial membranes. The materials selected for membrane and module manufacture were current state-of-the-art materials. Although the selection and use of the proper construction materials do not warrant good system integrity and quality, it is felt that a commercially useful tubular ultrafiltration system has been developed, thereby meeting the second and third objectives. This fact is substantiated by the positive results obtained from bench and pilot studies with actual process streams. Membrane performance and product quality in the applications which were investigated, compared will with results reported in the literature for commercial systems, despite the fact that no effort was made to develop membranes with optimum performance for each application.

The final objective of technology industrialization was met through the investigation of various applications, of which two in particular resulted in the construction of commercial plants. To date these plants have performed well in terms of membrane module integrity.

The development of the final membrane product can thus be seen as having successfully completed the full cycle from basic membrane and module development through pilot studies to commercial plant status.

-o O o-

LIST OF CONTENTS

CHAPTER ONE
OBJECTIVES

CHAPTER TWO
INTRODUCTION

CHAPTER FIVE
MEMBRANE EVALUATION

CHAPTER SIX
MODULE DESIGN AND EVALUATION

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

ABS	acrylonitrile/butadiene/styrene co-polymer
BSA	bovine serum albumin
CA	cellulose acetate
CFG	Ceres Fruit Growers
CFI	Ceres Food Industries
CIP	cleaning-in-place
COD	chemical oxygen demand
CSIR	Council for Scientific and Industrial Research
DAF	dissolved air flotation
DMA	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DMFE	dual media filter effluent
DMSO	dimethylsulfoxide
ICI	Imperial Chemical Industries
IPS	Institute for Polymer Science, Stellenbosch
MEMTUF	Membratek Tubular Ultrafiltration
MF	microfiltration
MLSS	mixed liquor suspended solids
MM	molecular mass
MMCO	molecular mass cut-off
NIWR	National Institute for Water Research
NMP	N-methyl-2-pyrrolidone
NTU	nephelometric turbidity unit
PAN	polyacrylonitrile
PAPI	polymer assisted phase inversion
PCI	Patterson Candy International
PEG	polyethyleneglycol
PES	polyethersulphone
PP	polypropylene
ppm	parts per million
PSF	polysulphone (also polybiphenylsulphone and polyarylsulphone)
PVA	polyvinyl alcohol
PVC	polyvinyl chloride
PVP	polyvinylpyrrolidone
QA	quality assurance
QC	quality control
RO	reverse osmosis
ROTAP	reverse osmosis permeate derived from tap water feed
SEM	scanning electron microscopy
SFW	Stellenbosch Farmers Winery
SLS	sodium lauryl sulphate
TCP	tricalciumphosphate
TDS	total dissolved solids
TFC	thin-film composite

TRO	tubular reverse osmosis
TS	total solids
TUF	tubular ultrafiltration
TWM	tube-winding machine
UASB	upflow anaerobic sludge blanket
UCC	Union Carbide Corporation
UF	ultrafiltration
UFM	ultrafiltration membrane
UFMs	ultrafiltration membranes
WPC	whey protein concentrate
WRC	Water Research Commission

308 membrane type
prepared from a casting solution containing
18,0% PES; 77,0% NMP and 5,0% PVP (32 000 MM) by mass.

309 membrane type
prepared from a casting solution containing
22,0% PES; 71,9% NMP and 6,1% PVP (32 000 MM) by mass.

713 membrane type
prepared from a casting solution containg
18,0% PES; 72,5% NMP; 8,0% PVP (32 000 MM); 1,0% 1,4-dioxane and 0,5% LiCℓ by mass.

719 membrane type
prepared from a casting solution containing
19,0% PES; 68,8% NMP; 10,0% PVP (32 000 MM); 2,0% DMF and 0,2% LiCℓ by mass.

FOREWORD

During the mid-seventies, the Water Research Commission (WRC) together with the Institute for Polymer Science (IPS), Stellenbosch and the National Institute for Water Research of the CSIR, decided that reverse osmosis (RO) could provide a solution to some of South Africa's water desalination problems. The IPS was sponsored by the Water Research Commission and the CSIR to develop the polymers and techniques required for membrane production. This resulted in the successful development of a tubular cellulose acetate membrane for reverse osmosis applications.

The need then arose to industrialise this membrane by a company willing to invest in further development in order to create a cost-effective support system for this tubular membrane. Ultimately an agreement was entered into by the WRC, IPS and Bakke Industries, Ltd., of Paarl (now Bintech), who were to develop the system.

By 1983 a module, meeting the design requirements, had been developed and sufficient knowledge had been gained in field tests to build a suitable system around the module to meet application needs.

During 1984 a number of significant contracts were awarded to Bintech , (Pty), Ltd. for the construction of tubular reverse osmosis (TRO) plants and the supply of tubular reverse osmosis membranes.

At about this time the market potential of ultrafiltration technology was realised by Bintech. Although the development of ultrafiltration technology had always been considered by the IPS, CSIR and WRC during the period of 1977 to 1981, little attention was given to the particular project. Fortunately for Bintech the IPS during 1984 and 1985 was involved with development of new generation membranes *i.e.* thin-film composites (TFC) in which an ultrafiltration type support membrane is used as substrate for the thin-film membrane.

Development of ultrafiltration (UF) technology received low-key priority until the end of 1985 when Bintech requested that the existing UF technology of the time should be transferred to industry for commercialisation.

In March 1986 these events resulted in the transfer of the author, who was actively involved in the TFC project at IPS at the time, to Bintech in order to assist in the simultaneous development of UF membranes, modules and systems, so as to reduce the time lag between the development and industrialisation phases.

This thesis documents the efforts made and techniques developed to achieve that goal.

CHAPTER ONE

OBJECTIVES

The events leading to the execution of the research work documented in this thesis, are given in the Foreword. The purpose of this chapter is to define the objectives of this thesis. The objectives were to fully commercialise the attributes and potential of tubular polyethersulphone ultrafiltration membranes through membrane development, adaption and modification of existing tubular RO module design, bench and pilot studies using real process streams and, finally, plant design.

1.1 ESTABLISHMENT OF MEMBRANE TECHNOLOGY

The first objective was to establish the technology required for the industrial production of commercially useful tubular ultrafiltration membranes (UFMs) made from polyethersulphone (PES). Tubular membranes had been made previously under laboratory conditions *(Jacobs, 1980; Jacobs et al., 1982)*. The manufacture of tubular ultrafiltration membranes from polyethersulphone on a commercial scale thus required the adaption of these laboratory techniques to suit industrial conditions. Membrane materials, as well as membrane manufacturing equipment and techniques which were used to accomplish this are discussed in CHAPTERS THREE and FOUR, respectively.

1.2 DEVELOPMENT OF TUBULAR ULTRAFILTRATION MODULES

The second objective was to incorporate the tubular PES ultrafiltration membranes into low-cost modules which were suitable for use in an industrial environment. This entailed modifying and reducing the cost of existing tubular reverse osmosis module technology *(Bakke, 1980)* to suit the ultrafiltration requirements. Ultrafiltration module design and evaluation are described in CHAPTER SIX.

1.3 EVALUATION OF ULTRAFILTRATION TECHNOLOGY

The third objective of this thesis was to evaluate the potential and performance of the membrane/module combination (ultrafiltration technology) through bench and pilot studies with real process streams. Results of these studies are given in CHAPTER SEVEN.

1.4 COMMERCIALISATION OF ULTRAFILTRATION SYSTEM

The final objective was to commercialise this ultrafiltration technology through the design, construction and commissioning of industrial-sized ultrafiltration systems. Commercial plants using the developed UF technology are discussed in CHAPTER EIGHT.

CHAPTER TWO

INTRODUCTION

2.1 INTRODUCTION TO ULTRAFILTRATION

2.1.1 HISTORICAL

The term ultrafiltration (UF) was first used by *Bechhold (1907, 1908)* in 1907 to describe the filtration of particles that were too small to be seen by ordinary optical microscopy despite the fact that the development and manufacture of the first synthetic membranes can be credited to Fick and Pfeffer respectively about 30 years earlier. During the 1920s a series of synthetic membranes were developed *(Elford, 1930; Zsigmondy and Carius, 1927)* for the ultrafiltration of particles with diameters of much less than a micrometres. For 40 years the process was rarely employed outside the laboratory. These early membranes were used primarily by scientists as a tool to study basic mass transport and thermodynamic phenomena and did not have any commercial significance.

The reason for this was mainly due to the low flux or filtration rates associated with these membranes *(Cheryan, 1986)*. It was only in the early 1960s after an asymmetric cellulose acetate (CA) membrane had been developed *(Loeb and Sourirajan, 1962)*, that membrane separation gained appeal as a method of fractionation. Asymmetric membranes which have a thin, dense membrane skin and a porous substructure, show significantly higher flux values and better flux stability than their symmetric counterparts who. This is because the pores of symmetric membranes soon become plugged with particles, since these membranes do not act as true surface filters due to their constant pore size throughout the entire thickness of the membrane.

Although these membranes were mainly intended for reverse osmosis (RO), the concept of an asymmetric membrane structure, which resulted in higher flux values, was readily adopted to prepare more porous membranes such as ultrafiltration membranes through the use of polyanion/polycation mixtures as a polymer matrix *(Blatt, 1976)*.

2.1.2 DEFINITION AND CLASSIFICATION

Traditionally, filtration implies the separation of components (usually solids) from a liquid. Membrane filtration, on the other hand, takes the concept further to include the separation of solutes from liquids and even the separation of gases.

For liquid applications, three membrane processes can be distinguished, *i.e.* microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO). All use a hydrostatic pressure-driving force and a specially structured polymeric film to separate solution components, the main difference being in the size of the components which can be rejected by the membrane *(Michaels, 1968)*. By definition, RO ideally allows passage only to water, while retaining all solutes. Ultrafiltration, on the other hand, retains suspended as well as dissolved macromolecules, separating them on the basis of differences in their physical size *(Parret, 1982)*. Microfiltration is intended to retain suspended solids in the 0,1 to 10 μm range *(Paulson et al., 1984)*.

The dimensions of particles which can be retained by ultrafiltration membranes range from about 1,5 nanometres (0,0015 μm) upwards *(Rohm and Haas, 1976)*. Separations requiring the retention of species with diameters less than 1,5 nanometers, which corresponds to a molecular mass of about 1 000, are considered to be applications of the related process, reverse osmosis (RO).

The upper limit in size of particles to which ultrafiltration is normally applied, is generally taken to be about 1 000 nanometres (1,0 μm). The main reason for this is that particles larger than one micrometre can usually be separated from solutions by established, low-cost methods such as sedimentation, microfiltration and ordinary filtration. The particle-size range to which the ultrafiltration process is applicable, is thus approximately from 2 to 1 000 nanometres (0,002 to 1,0 μm). Most commercially available UF membranes have effective pore diameters within the range 0,002 to 0,01 μm *(Beaton, 1977)*. Membranes with larger pores and which therefore give higher water fluxes are of little advantage, since it is the hydraulic resistance of the boundary layer of retained solids rather than the hydraulic resistance of the membrane itself, which limits the permeate flowrate. The reader is referred to FIGURE 2.1 for an illustration of the filtration spectrum.

Ultrafiltration is an economical mass separation technique that does not involve a phase change. It can therefore compete favourably with traditional phase-separation processes such as evaporation and spray-drying in terms of operating as well as capital cost *(Gekas et al., 1985; Uijttenboogaart, 1982; Nielsen, 1983* and *Veyre, 1984)*. Operating cost is mainly attributed to pumping cost, which makes UF considerably more attractive than thermal separation processes.

The process can be carried out at ambient temperature and the various chemical species to be separated are not chemically or physically altered. This is of special importance when temperature-sensitive materials such as whole egg and egg white have to be processed *(Cheryan, 1986)*.

In the past, the use of ultrafiltration was confined largely to the treatment of aqueous solutions. Recently, however, membranes which are resistant to many organic solvents have been described in the literature *(Iwama and Kazuse, 1982)*. A completely new and wide field for the application of ultrafiltration has thus been established, assuring an exciting future for the process.

2.2 MEMBRANE MATERIALS USED IN UF SYSTEMS

Ideally, membranes used for ultrafiltration should have high flux values, a sharp molecular mass cut-off *i.e.* the degree of ease with which a chemical species of a particular molecular mass passes through the membrane, as well as good mechanical, chemical and thermal stability *(Beaton, 1977)*. Additional requirements are good flux stability and long life expectancy.

It is obvious that a great deal is expected from a fragile membrane which is barely 0,2 mm in overall thickness. However, membranes prepared from synthetic polymers available today can satisfy all of these requirements to a high degree.

The first condition of high flux values is met by employing asymmetric membranes first developed by *Loeb and Sourirajan (1962)*. Such membranes have a thin, dense skin layer which is supported by a porous substructure providing mechanical strength.

These membranes act as true surface filters. Particles and molecules are retained at the surface where they are easily removed by shear forces resulting from the flow of the feed solution parallel to the membrane surface.

Asymmetric membranes are manufactured from a variety of polymers by the now generally employed phase inversion process *(Kesting, 1971)*. Specific membrane structures and characteristics can be obtained by changing the casting solution composition and casting parameters *(Strathmann, 1985)*.

The main criteria for membrane polymer selection are chemical, mechanical and thermal stability and ,of course, the ability to form an asymmetric (porous) film. In practice, the most widely used membrane polymers are cellulose acetate (CA), polyamides, polysulphones, polyimides and polyacrylonitrile-poly(vinyl chloride) copolymers as well as poly(vinylidene fluoride). A more extensive list of materials which have been investigated for use as membranes is given in the literature *(Lloyd and Meluch, 1985)*.

Some properties of UF membranes made from different materials are shown in TABLE 2.1 (adapted from *Cheryan, 1986; Iwama and Kazuse, 1982* and *Strathmann, 1984*).

TABLE 2.1 MATERIALS COMMONLY USED FOR THE MANUFACTURE OF UF MEMBRANES AND RESULTANT MEMBRANE PROPERTIES

POLYMER	TYPICAL MMCO VALUES	pH RANGE	MAXIMUM OPERATING TEMP (°C)	CHLORINE RESISTANCE (ppm)		ORGANIC SOLVENT RESISTANCE
				cont.	shock	
Cellulose acetate	1 000 - 50 000	3 - 6	30	1	50	poor
Polysulphone	5 000 - 50 000	1 - 13	100	50	200	fair
Aromatic polyamides	1 000 - 50 000	3 - 11	80	0	10	fair
PAN/PVC copolymer	30 000 - 100 000	2 - 12	50	fair	fair	fair
Polyimide	1 000 - 100 000	unknown	60	unknown	unknown	excellent

2.2.1 CELLULOSE ACETATE MEMBRANES

The first asymmetric UF membranes made from CA followed from the initial development of asymmetric membranes used in desalination *(Kesting, 1971)*. By varying the casting solution composition or casting procedure, CA membranes in a wide range of pore sizes can be made. Relatively high flux values can generally be obtained due to the hydrophilic nature of CA. Cellulose acetate, however, is chemically and thermally inferior to most synthetic membrane polymers with regard to resistance against deterioration *(Lonsdale, 1966)*.

CA membranes hydrolyse rapidly below pH 3 and above pH 6, the rate being accelerated drastically by an increase in temperature *(Pepper, 1980)*. The maximum operating temperature is generally limited to below 50 °C *(Lefebvre, et al., 1980)*. Also, being of organic nature, CA is more susceptible to bacterial attack than synthetic membranes. The main advantage of CA is that it allows the production of uniform, high quality membranes at low cost with relative ease. CA membranes are therefore still widely used today in both ultrafiltration and reverse osmosis.

2.2.2 POLYSULPHONE MEMBRANES

It was only in the early 1970s that useful asymmetric membranes were made from fully synthetic polymers *(Kesting, 1971)*. Polysulphone, in particular, emerged as a useful membrane material *(Cartwright, 1982)*. Due to their insensitivity to degradation, because of variations in pH and the presence of chlorine, even at elevated temperatures, polysulphone membranes have excellent chemical stability *(Johnson, 1986)*. Mechanical strength of polysulphone membranes compares favourably with that of CA membranes. Due to the synthetic nature of the polymer it is not prone to bacterial degradation.

Polysulphone membranes cannot be produced with as wide a range of pore sizes as CA for instance, due to the hydrophobic nature of the polymer. Membranes with low molecular mass cut-off values and simultaneous high fluxes are especially difficult to produce *(Strathmann, 1984)*.

2.2.3 POLYAMIDE MEMBRANES

Membranes made from this material are similar to those made from polysulphone *(McKinney, 1972; McKinney et al., 1974)*. Polyamide membranes with low molecular weight cut-off and high flux values can be manufactured due to the greater hydrophilic nature of polyamide compared to that of polysulphone *(Saier, 1977)*.

Polyamide membranes, however, are sensitive to chlorine attack even at low free chlorine levels (5-10 ppm) and are hydrolysed by alkaline solutions above pH 12 *(Kesting, 1977)*.

2.2.4 POLYACRYLONITRILE MEMBRANES

Because of the relatively hydrophobic nature of polyacrylonitrile, membranes of this type are limited to a lower molecular mass cut-off value of approximately 30 000. Membranes with lower cut-offs generally show very poor fluxes. In terms of chemical and thermal stability, polyacrylonitrile membranes show no advantage over membranes made from polysulphone. Their mechanical strength, however, is significantly lower than that of polysulphone or polyamide membranes. A positive feature of polyacrylonitrile membranes is that they can be dried out completely and rewetted without their filtration characteristics being changed. Membranes made from CA, polysulphone (depending on the technique of fabrication) or polyamide must be kept moist and prevented from losing the water in the polymer matrix. Drying of polysulphone membranes, for instance, leads to shrinking and cracking of the membrane. Lately, however, claims have been made that polysulphone membranes stored in a dried state, show filtration characteristics similar to identical membranes which were stored in a wet state *(Wafilin, 1983)*. Dry membranes offer advantages in storage, handling and shipping, since no provision need be made against the loss of moisture and preservation.

2.2.5 POLYIMIDE MEMBRANES

Membranes of this type have only recently appeared on the market *(Iwama and Kazuse, 1982)*. Polyimide membranes differ from ordinary synthetic membranes in that they are resistant to a broader range of organic solvents even at elevated temperatures. Previously, membrane processes were primarily restricted to the treatment of aqueous solutions. However, with the advent of this membrane type, a previously impossible application field for ultrafiltration has now become possible. Polymeric membranes generally fail to maintain their physical integrity in organic solvents due to their tendency to swell or dissolve. By using polymer materials that are more solvent resistant, it is possible to prepare ultrafiltration membranes for use in non-aqueous applications. Aprotic solvents, such as dimethyl formamide, dimethyl acetamide and dimethyl sulfoxide are not recommended for use, due to their tendency to swell the membranes.

2.3 FILTRATION CONCEPT

2.3.1 DEFINITION OF ULTRAFILTRATION

In ordinary depth filtration a solution is forced under pressure through a porous medium which retains some components (usually solids) present in the solution. UF is fundamentally different from depth filtration in two aspects. They are the mode of operation and the size of the average pore radii of the porous medium.

In ultrafiltration the flow of the solution which is to be filtered is parallel to the filtration medium (otherwise referred to as cross-flow), whereas in depth filtration the flow of the feed solution is perpendicular to the filter. Furthermore the average pore sizes of ultrafiltration membranes are roughly 1 000 times smaller than those of depth filters. The pores of an ultrafiltration membrane are on the scale of one nanometre and average pore diameters range from about one nanometre to roughly 10 nanometres. Hence, not only particulate matter, but also selected molecules can be removed and concentrated. Also most bacteria and viruses, which have a minimum size of some 20 nanometres, are rejected by UF membranes (refer to FIGURE 2.2)

Ultrafiltration therefore is in essence molecular filtration; it distinguishes between molecules of different sizes *i.e.* between those with different molecular masses. Dissolved molecules and suspended solids that are too large to pass through the pores in the membrane skin are rejected by ultrafiltration.

FIGURE 2.1

Filtration spectrum

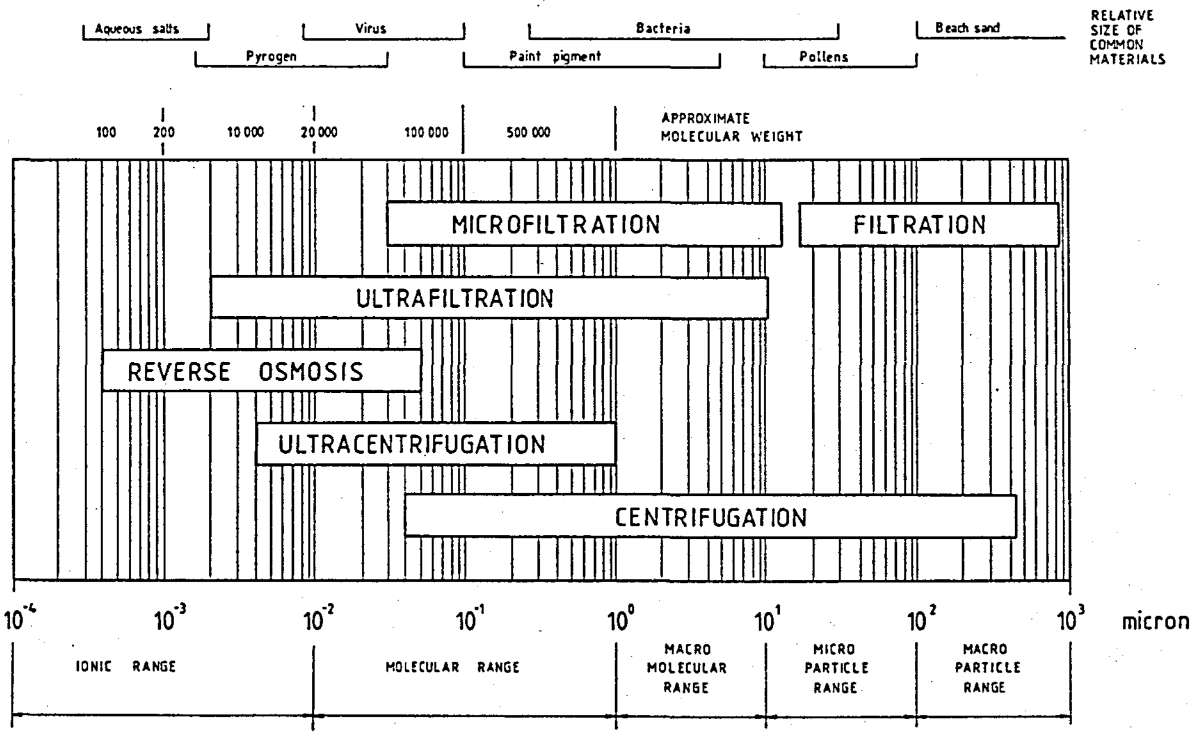
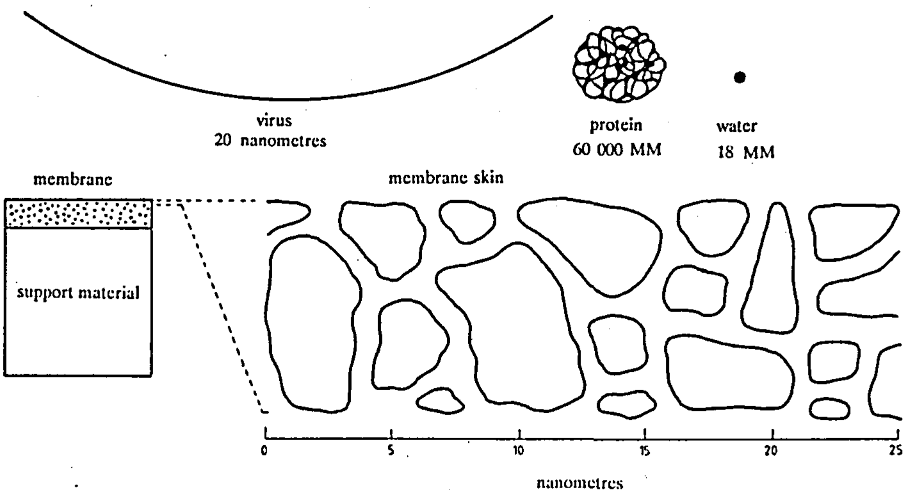


FIGURE 2.2

Graphic illustration of relative sizes between membrane pores and macromolecules



2.3.2 TRANSPORT ACROSS ULTRAFILTRATION MEMBRANES

In the description of transport phenomena across ultrafiltration membranes extensive use is made of various forms of the pore model *(Cheryan, 1986; Lonsdale, 1972; Nguyen et al., 1979).* The model is an extension of Darcy's law which is used to describe the convective transport through porous media. When applied to ultrafiltration, the transport relationships for solvent and solute flow through the pores in the membrane skin can be described as follows *(Blatt, 1976)*:

For solvent flux

$$J = \frac{B_p \, \Delta P}{\Delta x} \tag{1}$$

where

J = solvent flux
B_p = specific permeability of the membrane to solvent
ΔP = hydraulic pressure difference
Δx = membrane thickness

For solute that is carried convectively with solvent through the pores that are large enough to allow passage of the solute molecules

$$J_1 = C_B \, (1-\sigma) \, J \tag{2}$$

where

J_1 = solute flux
C_B = bulk concentration of solute
$(1-\sigma)$ = fraction of the solvent flux carried by pores large enough to pass the solute

mass balance dictates that

$$J_1 = J \, C_P \tag{3}$$

where

C_P = concentration of solute in the permeate

therefore

$$\sigma = 1-(C_P/C_B) \tag{4}$$

2.3.3 FACTORS WHICH AFFECT TRANSPORT

2.3.3.1 Membrane morphology

One of the factors which influences the rate of permeability of the membrane is related to the membrane structure. Since solvent transport through the membrane consists of viscous, pore flow, the maximum attainable permeation rate at a specific applied pressure and temperature is limited by membrane morphology. The inherent permeability of a membrane for water is usually expressed as a pure water flux value determined at specific test conditions. The pure water flux value provides some indication of the actual membrane structure. A high pure water flux value is indicative of a relatively porous membrane and a low value is associated with a less porous membrane. Pure water flux is discussed in more detail in section 5.1.

2.3.3.2 Membrane thickness

Another factor which affects the rate of permeation through a membrane is the overall thickness of the membrane itself. Since the membrane provides resistance against flow, the permeation rate is indirectly proportional to membrane thickness. This fact follows directly from equation *(1)* in section 2.3.2. Thus, in theory, one would strive to fabricate as thin a membrane as possible in order to maximise permeation rate. In practice, however, membranes are usually made thick enough to facilitate mechanical integrity and to ensure durability. The discovery of a technique by *Loeb and Sourirajan (1962)* for the preparation of asymmetric membranes which have high solvent permeability, can be considered to be a breakthrough in this respect. The thin, dense membrane skin which is the active, working part only contributes to a fraction of the overall membrane thickness (the rest being made up by the porous substructure), thereby reducing the resistance to solvent flux.

2.3.3.3 Concentration polarisation

The phenomenon of conentration polarisation can be described in terms of the film model and boundary layer theories *(Drioli and Bellucci, 1978; Paperfuss et al., 1978)*. During ultrafiltration solute is brought to the membrane surface by convective transport (refer to equation *2* in section 2.3.2). A portion of the solvent (permeate) is then removed from the solution (feed stream) through the membrane. This leads to a higher local concentration of solute at the membrane surface as compared to the bulk. It is immaterial whether the solute is rejaected partially or completely by the membrane skin. This build-up of solute is referred to as the concentration boundary layer. Initially, due to the convective transport of solute to the membrane surface, a steep concentration gradient results in the boundary layer. Due to this concentration gradient diffusional effects will cause a back-diffusion of solute into the bulk (see FIGURE 2.3).

A steady state will eventually be reached where the convective transport of solute by solvent is balanced by the back-diffusive transport of solute *(Blatt, 1976)*. This can be described in mathematical terms as follows

$$J_1 C = D\ (dC/dx) \qquad (5)$$

where

J_1 = solute flux
C = local concentration of membrane retained solids
dC/dx = concentration gradient
D = diffusion coefficient

Integration and specification of boundary conditions yields

$$J_1 = D \ln (C_G/C_B)/\delta \qquad (6)$$

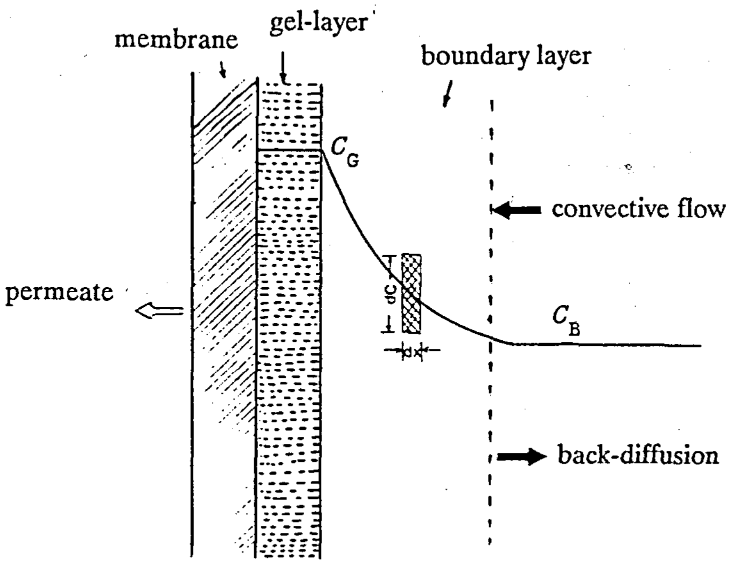
where

C_G = solute concentration at upper limit (gel concentration)
C_B = bulk concentration of solute
δ = boundary layer thickness

The condition where the convective flow of solute to the membrane surface exceeds the rate of back-diffusion to the bulk stream, is referred to as concentration polarisation. Concentration polarisation can change the retention characteristics of the membrane through gel-layer formation *(Capannelli et al., 1983)* at the membrane surface (see FIGURE 2.3) which reduces permeability, but can also give rise to undesirable phenomena such as the precipitation of solute at the membrane surface *(Nakao et al., 1982)*

It is usually endeavoured to limit the degree of concentration polarisation in order to obtain maximum membrane flux values. This can be achieved by enhancing the mass transfer rate (diffusion coefficient) through mixing and by reducing the thickness of the boundary layer. At high linear flow velocities the boundary layer is sheared off to a large degree due to an increase in turbulence, thus reducing concentration polarisation. Feed solution temperature also has a pronounced effect on the filtration rate of UF membranes. An increase in feed solution temperature leads to higher flux values since the viscosity of most liquids decreases at elevated temperatures, leading to more turbulent flow conditions with a resultant decrease in concentration polarisation *(Nakao et al., 1981)*.

FIGURE 2.3
Boundary layer concept



2.4 TYPES OF UF MODULES

For the successful use of UF as an efficient separation process, the design of the module containing the membrane or membranes, as well as plant design, are as important as the selection of the proper membrane.

Since concentration polarisation is governed by fluid dynamics, the extent of concentration polarisation is influenced by factors which have an effect on fluid dynamics such as module configuration *(Kesting, 1971)*. The gel-layer which forms as a result of concentration polarisation can drastically alter the UF properties of the membrane. Not only does gel-layer formation reduce the filtration rate since the gel-layer acts as a secondary membrane which offers major resistance to flow *(Porter, 1981)*, that is the economics of the process, but it can also change the separation characteristics of the membrane. One of the most significant aspects in the design of an UF module is the control of the feed flow distribution at the membrane surface *(Shen and Probstein, 1977)*.

At present several UF module designs are being utilised; these show significant differences in the feed flow distribution, operating pressure, capital and operating costs. The more important module configurations used in large scale commercial UF units are summarised in TABLE 2.2.

TABLE 2.2 RELATIVE COMPARISON OF ULTRAFILTRATION MEMBRANE MODULE CONFIGURATIONS

MODULE TYPE	PACKING DENSITY (m^2/m^3)	CAPITAL COST	OPERATING COST	FLOW CONTROL	EASE OF CLEANING
Tubular	25 - 50	High	High	Good	Good
Plate-and-frame	400 - 600	High	Low	Fair	Poor
Spiral Wound	800 - 1 000	Very low	Low	Poor	Poor
Hollow Fibre	600 - 1 200	Low	Low	Good	Fair
Grooved Rods	200 - 300	Low	Low	Poor	Fair

Each of these configurations has distinct advantages and disadvantages. As a result each of the configurations has become associated with certain application fields where the advantages of the particular device are maximised.

2.4.1 TUBULAR MODULE

The tubular module was first developed for RO operations. This system provides a good measure of control of membrane fouling and concentration polarisation. The main reason for this is that tubular systems are tolerant towards suspended solids in the feed solution. This system is very flexible with regards to control of feed flow velocity, which influences the degree of concentration polarisation. When excessive membrane fouling occurs, mechanical cleaning of the system is possible with the aid of sponge balls *(Rekers and Gons, 1981)* an advantage no other system offers. The disadvantages of the tubular system are relatively high capital cost and low ratio of membrane-area-to-system-volume. While tubular RO modules have been replaced to a large extent by hollow fibre systems because of high investment and operating costs, they are still widely used in UF.

In the tubular configuration, a porous support tube is lined on the inside with a membrane. The pressurised feed solution flows down the tube bore, the product solution permeates the membrane and is collected on the outside. Usually a number of tubes are housed in a bundle in a shroud which acts as a pressure and permeate collection vessel. Tubular membranes may be connected in series or in parallel array. Tube diameters vary, in general, from 6 to 25 mm, while length ranges typically from 1 to 6 metres. Tubular systems are typically operated at linear flow velocities of 1 to 5 m s^{-1} , *i.e.* under turbulent conditions (Reynolds numbers usually greater than 10 000). Relatively high pressure drops (600 to 1 000 kPa) are encountered per module, which contribute to high pumping cost.

Tubular UF systems are widely used in the food industry and for the treatment of effluent *(Hedrick, 1983)*, because of the high fouling nature of the feed solutions associated with these applications. The tubular module concept is shown in FIGURE 2.4. Some of the major tubular membrane module manufacturers are Abcor (U.S.A.), Patterson Candy International (United Kingdom), Wafilin (Netherlands), Western Dynetics (U.S.A.) and Nitto-Denko (Japan).

2.4.2 GROOVED ROD MODULE

The rod membrane module is similar to the tubular configuration, except that the membrane is situated on the outside of the support and that the permeate flows in the reverse direction. Examples of such modules are the Rodyne™ and Ultradyne™ equipment manufactured by Western Dynetics, U.S.A. The module consists of grooved rods coated on the outside with an asymmetric membrane. Usually the grooved rod is first covered with a braided material which supports the membrane and keeps the grooves in the rod open to facilitate permeate flow. The concept of this module is shown in FIGURE 2.5.

Membrane area per unit volume of this system is relatively high, but control of concentration polarisation is not as easy as in tubular systems.

2.4.3 PLATE-AND-FRAME MODULE

Plate-and-frame membrane systems were amongst the very first to be utilised in large scale RO and UF applications *(Madsen, 1977)*. The design has its origin in the conventional filter-press concept. The membranes, the porous membrane support and spacer material which facilitate permeate flow, are clamped together in a sandwich formation much as in a plate heat exchanger. The variety of designs which employ this concept vary mainly in the design of the feed-flow channels.

Although this system offers a large membrane area per unit volume, plugging of flow channels can be a serious problem, especially with solutions containing suspended solids. Cleaning usually requires dismantling of the module which is a time-consuming and tedious task.

Capital cost for this configuration is comparable to that of the tubular system, while operating costs are somewhat lower. Major manufacturers of plate-and-frame membrane modules are Dorr-Oliver (U.S.A.), De Danske Sukkerfabrikker (Denmark) and Rhone-Poulenc (France).

2.4.4 HOLLOW FIBRE MODULE

Hollow fibre membranes can be manufactured from a variety of polymers by the dry-jet wet spinning process *(Cabasso, 1980)*. In the process a spinneret is located above an exterior coagulation bath and upon submersion of the fibre, the nascent membrane is transformed into a hollow fibre. The thin, dense skin on the inside is supported by a spongelike outer substructure *(Rohm and Haas, 1976)*. The fibres are thus self-supporting structures and do not require additional support or backing as tubular membranes do. The inside diameters of the fibres are typically 0,5 to 1,0 milimetres *(Breslau et al., 1977)*. Hollow fibres intended for UF applications should not be confused with those used in RO applications where the dense skin is on the outside of fibres. Hollow "fine" fibres used in RO applications are also smaller in diameter by an order of magnitude to withstand the higher operating pressures *(Applegate, 1984)*.

The module system consists of a bundle of a large number of hollow fibres in a shell with epoxy encased ends. Feed solution enters the module at one end and flows through the bores of the fibres. Matter rejected at the skin of the membrane fibres and leaves the fibre bores as a concentrate at the other end. Permeate flows through the substructure and is removed through the filtrate port. The general configuration of the system is shown in FIGURE 2.6. Hollow fibre membrane modules are manufactured by Amicon (U.S.A.) and Romicon (U.S.A.) amongst others.

The system provides good control of concentration polarisation and a very high membrane surface area per unit volume. Operating pressure, however, is limited which is sometimes a disadvantage *(Cheryan, 1986)* and the system is relatively sensitive to operating errors. Hollow fibres operate in the laminar flow region (Reynolds numbers of 500 to 3 000) due to lower operating velocities (0,5 to 2,5 m s^{-1}) which are required to obtain high shear rates in the fibres, since the flow channels are very small.

2.4.5 SPIRAL WOUND MODULE

The spiral wound module is widely used in RO for the desalination of sea water and brackish water *(Applegate, 1984)*. In principle it is a plate and frame system that has been rolled up. Membranes are cemented to each side of a porous paper or cloth. Then the double membrane is wound with a spacer of plastic netting around the permeate collection pipe. The feed stream enters the module in a direction parallel to the permeate pipe. Permeate flows along the spiral path of the porous supporting material and is collected in the central permeate pipe.

In appearance the spiral wound module resembles a swiss roll. The reader is referred to FIGURE 2.7 for a simple schematic diagram of a spiral wound module. Membrane surface per unit volume is high and capital and operating costs are low. Unfortunately, concentration polarisation effects are difficult to control in these modules. Spiral modules are more susceptible to fouling than tubular units *(Tang et al., 1981)* mainly due to the the lack of turbulence in the ill defined flow channel which can result in the stagnation of the feed solution *(Cheryan, 1986)*. Spiral wound membrane modules are primarily manufactured by Osmonics (U.S.A.), Abcor (U.S.A.) and Permionics (India).

FIGURE 2.4
Tubular module concept

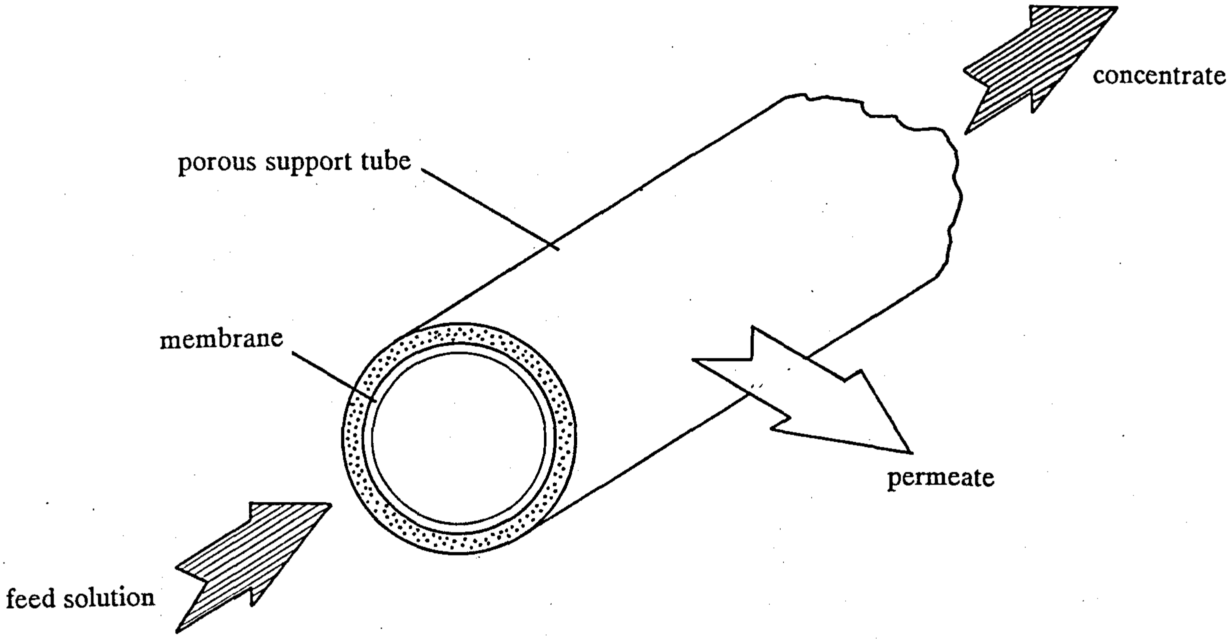


FIGURE 2.5
Grooved rod module concept

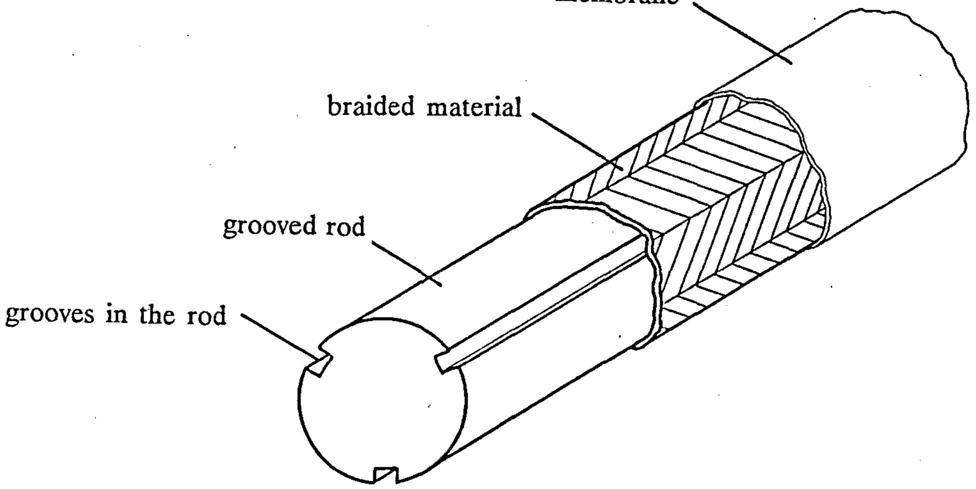


FIGURE 2.6
Hollow fibre module concept

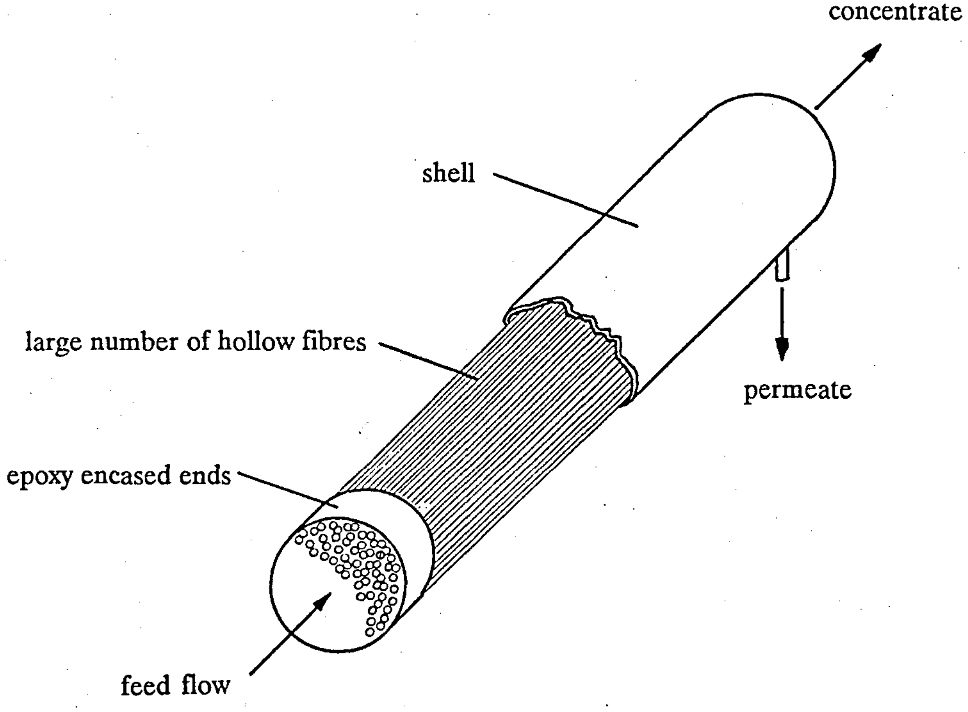
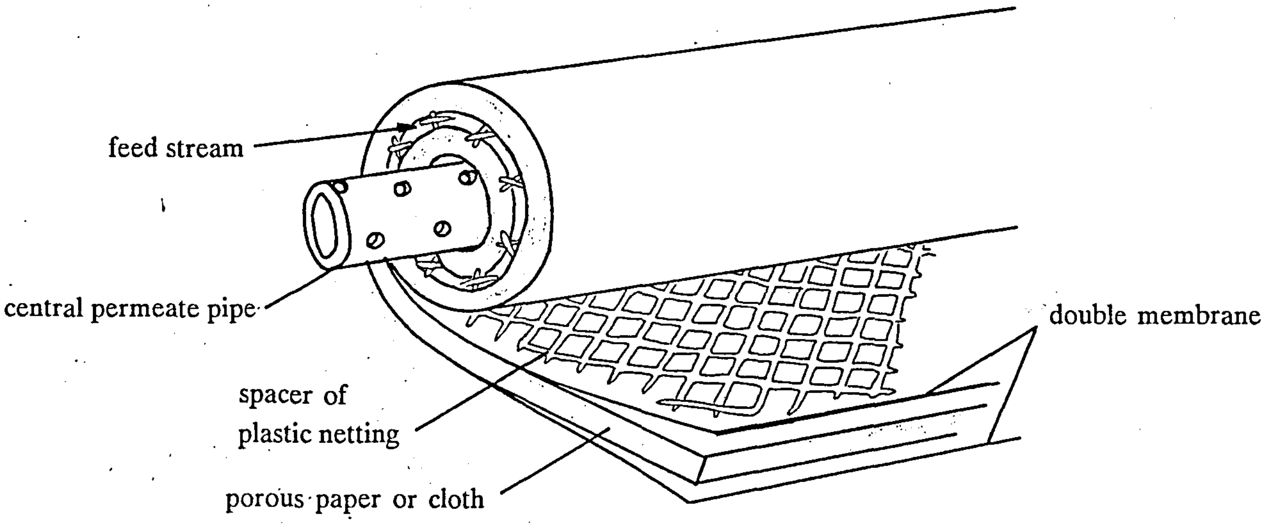


FIGURE 2.7
Spiral wound module concept



2.4.6 COMPARISON OF ULTRAFILTRATION MODULES

Because of the variation in design and performance of UF systems, comparison of capital and operating costs is difficult.

In general, the tubular module is the most expensive in terms of capital and operating costs due to the low packing density (membrane surface area-to-volume ratio) and high pressure drops associated with this module type *(Cheryan, 1986)*. Nevertheless tubular systems are widely used in applications where fouling is a major factor, where product value is high, and system flexibility is a requirement. Here the control of feed flow distribution (thus concentration polarisation to a degree), the proven system reliability and the ability to handle feeds containing suspended particles, more than compensate for the relatively high capital and operating costs *(Goldsmith, 1975)*. As such, tubular systems find extensive use in the food industry and in effluent treatment *(Hedrick, 1983)*.

The use of plate and frame systems is fairly widespread in the dairy industry, despite the high capital costs of these systems. This is due to the significant advantages offered by this design in terms of easy membrane replacement and high operation reliability *(Madsen, 1977)*.

Hollow fibre and spiral wound systems have also been used successfully for the treatment of wastewater. Although a prefiltration procedure is generally required, their relatively low capital and operating costs make these systems attractive for this type of application *(Wysocki, 1976)*.

In conclusion, because of the diverse nature of UF applications, one module configuration does not dominate the application field and each system seems to have found its own *niche* where it is applied successfully. The tubular system can be considered to offer the most flexibility in terms of operation and has a very wide range of applications. This can be attributed to the open and well defined flow channel associated with this design. Concentration polarisation can be controlled by simply increasing the flow velocity inside the tubes which results in a decrease of the gel-layer thickness *(Cheryan, 1986; Lonsdale, 1972)*. The tubular membrane module also offers the advantage of mechanical cleaning by sponge balls and feed flow direction reversal to control membrane fouling. The major disadvantage of the tubular module is its high capital cost. A reduction in cost of the support technology of tubular modules to capital cost values of spiral modules would serve to capitalise to a greater extent on the advantages mentioned above.

2.5 SOUTH AFRICAN MARKET FOR ULTRAFILTRATION

Numerous applications of UF technology exist in the literature which cover a wide range of processes concerned with the concentration and/or clarification or the recovery of some valuable substance. Mainly two types of applications classifications can be distinguished *(Beaton, 1977)*; those that are concerned with the concentration of colloidal particles and those that treat soluble macromolecules. Examples of each type are given in TABLES 2.3 and 2.4 respectively.

In South Africa the possible applications for UF are numerous and range from water treatment to use in the food industry. Some areas for the application of ultrafiltration technology which were identified by the author to have potential market value, are listed in TABLE 2.5.

In spite of this seemingly vast number of applications, the utilisation of UF technology in South Africa is virtually non-existent. This can be attributed to the fact that no UF membranes or systems are manufactured locally. At present all UF systems used in laboratory and industrial applications have to be imported from either Europe, the United States or Japan. As such, the capital cost of these systems is generally regarded as too high by the prospective user to warrant their utilisation in competition with conventional filtration and traditional concentration methods. Also technical back-up and service are usually poor since representation of such suppliers in our country is limited to agencies without manufacturing facilities. Another reason is that in most industrial sectors, such as the dairy industry, the various processing plants (dairies) are small and widespread in a geographical sense. The use of numerous small membrane separation plants spread over a wide area would not seem attractive because of the capital cost and distances involved. Even if the various plants (dairies) could be combined, the total size of the particular market is usually not large enough to enable the full exploitation of all the advantages of membrane separation processes, because of the high capital cost of imported systems, since an adaptation of the traditional process is normally required which adds to the cost.

TABLE 2.3 REPRESENTATIVE EXAMPLES OF UF APPLICATIONS (COLLOIDAL PARTICLES) ADAPTED FROM BEATON (1977)

APPLICATIONS CLASSIFICATION	EXAMPLE OF APPLICATION
Pigments and dispersed dyes	Reclamation of electropaints Concentration of pigments in printing effluents Purification of organic pigment slurries
Oil in water emulsion	Concentration of cutting oils from machining operations
Polymer dispersions	Concentration of emulsion polymers from reactors and washings
Metals/non metals	Concentration of silver from photographic wastes Concentration of activated carbon slurries
Micro-organisms	Retention of microbiological solids in activated sludge processing Concentration of viral cultures
Plant/animal	Retention of cell debris in fruit juices
Cellular materials	Retention of cellular matter in brewery/distillery wastes

TABLE 2.4 REPRESENTATIVE EXAMPLES OF UF APPLICATIONS (SOLUBLE MACROMOLECULES)

APPLICATIONS CLASSIFICATION	EXAMPLE OF APPLICATION
Proteins	Concentration of enzymes Concentration of casein/whey Concentration of gelatin/blood Concentration of egg albumen
Polyphenolics	Concentration of lignosulphonates
Polysaccharides	Concentration of starch effluents

TABLE 2.5 ULTRAFILTRATION APPLICATIONS IN S.A.

FOOD INDUSTRY

Fruit juice clarification - apple, grape, pear, guava, loganberry, *etc.*
Concentration of whole egg
Gum concentration - pectins, gelatine
Sugar refining
Whey concentration/cheese production
Production of pure water

APPLICATIONS OTHER THAN FOOD

Gelatine concentration (abattoir effluents)
Sewerage effluent clarification
Dye house effluent clarification
Protein concentration of potato wastewaters
Water purification, removal of bacteria, pyrogens *etc.*
Tanning industry effluent clarification
Concentration of proteinaceous egg wastes
Reclamation of bio-mass from anaerobic sludge
Sludge dewatering

2.5.1 UF IN S.A. FOOD INDUSTRY

At present the only application which shows immediate market potential for UF technology in the S.A. food industry, is the clarification of fruit juices in the beverage industry. As far as could be ascertained in a survey conducted by the author, only two industrial-sized UF plants are presently in operation in the food industry in this country. Both of these are utilised for the clarification of fruit juices and have an approximate capacity of 240 $m^3 day^{-1}$ of clarified juice. The clarification of apple juice is reported in the literature *e.g.* by *Nielsen (1983)* and *Veyre (1984)*. According to Nielsen, running costs are about 30% of those of the traditional process. Yields are reported to be at least 97% by straightforward ultrafiltration and up to 99,4% can be achieved by introducing diafiltration during the process. The equipment usually has a pay back period of about 18 months. A pilot plant study on the clarification of fruit juice and sludge with UF systems developed by the author is described elsewhere in this thesis.

According to the Animal and Dairy Science Research Institute *(Downes, 1987)*, Irene, no UF plants are presently employed commercially in the South African Dairy Industry. In Europe and America most milk-producing countries now have industrial plants for membrane filtration of milk and/or whey. According to *Hanemaaijer (1985)* about 100 000 m^2 of ultrafiltration membrane had been installed for dairy applications by the end of 1983, out of which 80 000 m^2 were used for whey processing and 20 000 m^2 for milk. *Maubois (1984)* estimates that the overall UF membrane area was further increased to a total of about 120 000 m^2 by the end of 1984.

The possibility of concentrating cheese whey to yield whey protein concentrate with the aid of locally manufactured UF membranes, is illustrated elsewhere in this thesis. Technologists in the local dairy industry are well aware of the advantages of UF and RO processes, but are doubtful of the cost of membrane replacement if plant operation is left to semi-skilled labour *(Venter, 1988)*. As such, the opportunity for employing membrane processes in the South African Dairy Industry exists, but overcoming this reservation and changing the attitude of the industry towards the use of membrane processes will require considerable time and effort.

One other application for UF which shows reasonable market potential, is in the stabilisation of wine and grape juice. UF offers the possibility of eliminating the high-molecular-mass substances (proteins) which are responsible for protease activity in must and wine. By using membranes with a relatively low molecular mass cut-off, these proteins can be removed, to produce a stable and smoother coloured product.

The Cape wine industry shows enthusiasm towards the employment of local membrane technology, especially since a locally designed and manufactured tubular RO plant for the recovery of tartrates on an industrial scale was commissioned successfully towards the end of 1986.

2.5.2 OTHER S.A. MARKETS FOR UF TECHNOLOGY EXCLUDING FOOD APPLICATIONS

Outside the food application area, the biggest opportunity for UF technology utilisation is probably in the purification of water and effluents. Various industries (*e.g.* dye houses and canneries) require good quality water during certain production steps. Variations in water quality can sometimes not be prevented when traditional filtration methods (*e.g.* sand filters) are used. With UF, water of constant and high quality can be obtained, which occasionally is of critical importance. In the textile industry, for example, a constant supply of water quality ensures that colour variations in consecutive dye solution batches are kept to a minimum. UF could also be used to reduce the chemical oxygen demand (COD) value of secondary sewerage and other effluents to lighten the load on municipal treatment works and to prevent the imposition of penalties on companies who are presently not meeting COD specifications.

In order to break into the water treatment market, UF will have to compete with conventional filtration methods and microfiltration and as such will have to be competitively priced. System design, performance and cost reduction exercises for water clarification applications are described in section 7.2 of this thesis.

CHAPTER THREE

MEMBRANE MATERIAL SELECTION AND CHARACTERISATION METHODS

3.1 INTRODUCTION TO MEMBRANE MATERIAL SELECTION

The wide acceptance of ultrafiltration as a new chemical unit operation is the result of successive developments of the following elements (which were discussed in CHAPTER TWO):

i) polymeric membranes (materials and morphology);
ii) various membrane configurations;
iii) membrane devices and systems.

In order to narrow the scope of the present discussion, an ultrafiltration membrane (UFM) will be defined as an anisotropic film layer, having a tight, but porous upper surface (generally referred to as skin) extending from a highly porous, spongy substructure. The bottom face is also highly porous and is, unlike the upper face, an integral extension of the membrane substructure. A typical cross section of an UFM is shown in FIGURE 3.1.

The polymer in this asymmetric structure serves in two capacities, the upper skin is the permselective barrier and the substructure is its mechanical support. Unlike the reverse osmosis membrane employed for water desalination, the skin of an UFM permits viscous flow.

The properties of UFMs with regard to their structure should be divided into:

i) skin characteristics (pore density, dimensions, orientation and shape, and skin topography);
ii) substructure (porosity, channel tortuosity and macrovoids);
iii) bottom face (openings in the bottom porous skin).

The chemical nature of an UFM should be identified with respect to solvent and chemical resistance (pH, oxidising agents), surface activity (affinity for Lewis acids or bases) and its wettability (hydrophilic/hydrophopic balance).

Regarding the membrane permselectivity, the surface pore-shape and chemical entity are major influences. The chemical entity may be visualised as a sphere having the pore's surface radius and centre. The chemical entity of the skin pores would exert decreaseing influence over membrane permselectivity as pore radii increase. For practical purposes one may conclude that permselectivity in UFMs is the result of pore/solute interaction as opposed to membrane material/permeate interaction in RO membranes.

These divisions provide simple criteria for the selection of materials from which UFMs may be constructed. As such, one can conclude that any material yielding an anisotropic morphology and neutral membrane surface, may be used to fabricate UFMs which should have more or less the same permselectivity for aqueous solutions. Thus cellulose esters, polysulphones, poly(vinylidene fluoride), poly(dimethylphenylene oxide), poly(acrylonitrile) and others which can be solution-cast or spun to provide an UFM by the phase-inversion process, can be tailored to yield the same transport properties and permselectivity *(Kesting, 1985; Strathmann, 1985)*. The general method for the manufacture of polymeric membranes consists of dissolving the polymer in a suitable solvent and casting or spinning the resultant solution to obtain the required membrane type (flat sheet, tubular or hollow fibre). This is accomplished with the aid of casting equipment and the so-called phase-inversion process.

Casting equipment is not commercially available and is highly individualistic. The equipment is usually designed and manufactured by the membrane manufacturers themselves.

There are three basic mechanisms of phase-inversion by which the polymer solution is inverted into a three-dimensional matrix in which the polymer is the continuous phase. They are the **dry**, the **wet** and the **thermal phase-inversion process**. These mechanisms are described in detail in the literature *(Kesting, 1985)* and will be defined only briefly here.

(i) The **dry process** involves complete evaporation of the solvent in the polymer solution with subsequent precipitation of the polymer.
(ii) During the **wet process**, the solvent is interchanged with non solvent, leading to the coagulation and gelation of the polymer.
(iii) In the **thermal process**, a polymer solution is prepared at a high temperature and upon subsequent cooling the polymer precipitates from the solution.

The wet phase-inversion process was used for the development and production of ultrafiltration membranes, described in this thesis, since the author had previous experience with the methods and equipment required for this process.

3.2 MEMBRANE MATERIALS

3.2.1. MEMBRANE MATERIAL REQUIREMENTS

Before deciding on the actual materials which are to be used for the fabrication of ultrafiltration membranes, certain factors have to be considered. The most important are :

3.2.1.1. *Hydrophilic or hydrophopic characteristics*

Surface tension and contact angle, generally referred to as capillarity, combine to prevent spontaneous wetting of membranes unless the filter material is hydrophilic. Unfortunately, most synthetic polymers suited for membrane fabrication are relatively hydrophobic. Since an increase in the hydrophilic property of a membrane implies an inherent increase in membrane flux for aqueous solutions, one would strive to make the synthetic membrane as hydrophilic as possible. Fortunately, by careful selection and modification of the functional groups on the polymer backbone, most of the synthetic membrane polymers can be rendered more hydrophilic *(Drzewinski, 1985)*.

3.2.1.2. *Mechanical strength*

The polymer matrix of which the membrane consists must have sufficient mechanical strength to withstand compaction and abrasion under high pressure, temperature and prolonged use, to give an economic membrane lifetime. This is in part a function of membrane material choice and casting solution composition.

3.2.1.3. *Chemical and thermal resistance*

Materials having wider ranges of chemical resistance are generally preferred, as they give membranes with greater operational flexibility *(Johnson, 1986)*. Often membranes are expected to operate at temperatures above ambient. Care must be taken to exclude materials which have poor resistance to high temperatures when the membrane is expected to operate at elevated temperatures.

3.2.1.4. *Sterilisability*

Approval by the governing controlling body for food and drugs, as well as sterilisability, determine whether a membrane can be used in the food or pharmaceutical industries. The membrane material is therefore expected to withstand treatments such as steam or chlorine sterilisation.

3.2.2. MEMBRANE POLYMER

The chemical, mechanical, thermal and hydrolytic stabilities of the polysulphone polymers was emphasised in CHAPTER TWO section 2.2.2. Due to increasing demands for high stability, polysulphone membranes for both UF and RO (as supporting membrane for thin film composite membrane manufacture) are commercially produced by several manufacturers. Although polysulphones are relatively hydrophobic, which makes the production of UFMs with low cut-off and high flux values difficult, the material is preferred because the phenyl ether and phenyl sulphone groups have high thermal and oxidative stability, producing long-term stability in membranes during use *(Deanin, 1972)*.

There are three major types of polysulphone polymers currently available commercially, although others are being developed and are starting to enter the market *(Wood, 1987)*. These are marketed under the trade names UDEL™ (poly bisphenol-A sulphone), RADEL™ (polyarylsulphone) and VICTREX™ (polyarylethersulphone, hereafter referred to as polyethersulphone). The materials are available in different grades, the first two being supplied by Union Carbide Corporation (UCC) and the third by Imperial Chemical Industries (ICI). The chemical structures of the three polymers according to *Ballintyn (1982)* are given in FIGURE 3.2.

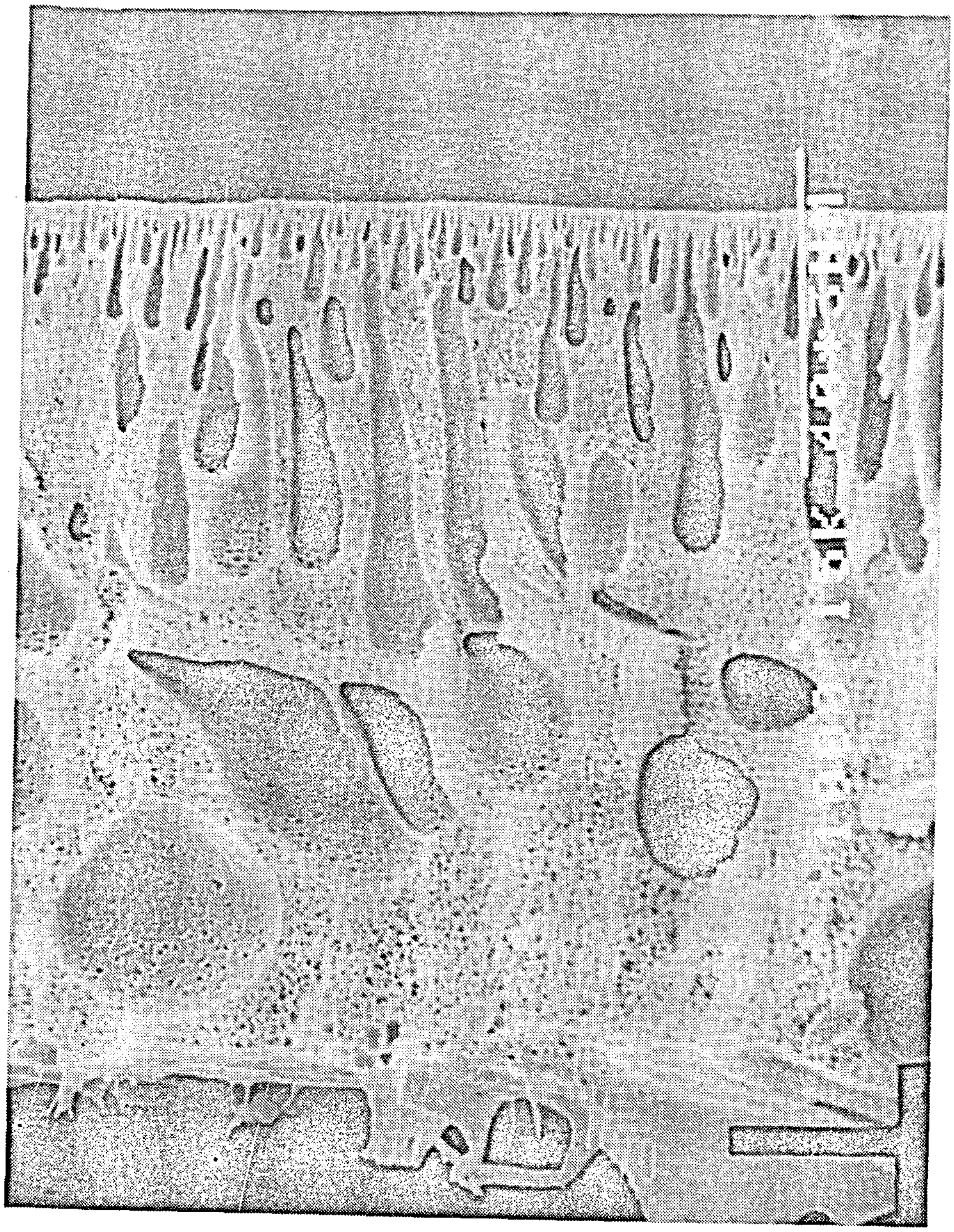


FIGURE 3.1

Scanning electron micrograph depicting a cross-section through a typical ultrafiltration membrane (magnification 750 X). The thin, but dense membrane skin can be seen at the top. The skin is supported by the porous substructure which accounts for practically the entire thickness of the membrane. The substructure shows "finger"-like cavities resulting from a fast precipitation rate. The pore diameter increases from the top to the bottom side of the membrane which is typical of asymmetric membranes.

In contrast to many studies on polysulphone (PSF) membranes regarding stability and preparation *(Nishimura, 1977; Cabasso, 1977; Tweddle, 1983)*, little work has been reported on UFMs made from polyethersulphone (PES) which should be more promising than PSF due to its higher thermal stability (higher glass transition temperature)*(Wood, 1987)*. Also according to *Dreger (1978)* the equilibrium water absorption at 20 °C for VICTREX™ is highest (2,1%) when compared with that of RADEL™ (1,3%) and UDEL™ (0,85%). Equilibrium water absorption data may be regarded as a measure of the relative polar nature of the polymer.

VICTREX™ is thus the least hydrophobic of the three which theoretically should aid in the production of membranes with higher flux values. Bearing in mind the points stated above, it was decided to select polyethersulphone (VICTREX™ 4800 G) supplied by ICI, United Kingdom, as the polymer for UFM development and fabrication.

3.2.3. POLYMER SOLVENT

When a suitable solvent for the polymer which is to be used in the preparation of the ultrafiltration membrane (UFM) casting solution is chosen, the following guidelines are applicable *(Wafilin, 1983)*:

The boiling point of the solvent in question should be above 100 °C and the solubility parameter thereof above 8, preferably between 10 and 12,5. The Hildebrandt solubility parameter δ_t with its partial parameters δ_d, δ_p and δ_h representing the dispersive, polar and hydrogen bonding contributions to cohesive energy is defined as follows *(Barton, 1983)*

$$\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{0,5}$$

The solubility parameter is an indicator of the nature and strength of the physio-chemical interactions between the membrane polymer and the solvent *(Hansen, 1970)*. These interactions determine macromolecular conformation in solution, polymer precipitation rate, solvent/non-solvent exchange rate and ultimately membrane structure and performance *(Kamide and Manabe, 1985)*.

The use of a high-boiling solvent prevents evaporation immediately after extrusion of the polymer solution and allows the solvent to be extracted only after submersion of the membrane in the coagulation bath. In this way the void size throughout the entire thickness of the membrane can be kept nearly constant. Membrane structures of this type are less susceptible to compaction under pressure than are membranes with large, irregular macrovoids in their substructure.

Another requirement of a suitable solvent is that it should be water miscible, since the UFMs are prepared by the wet phase-inversion process, in which the use of an inexpensive non-solvent for the polymer would be a definite cost advantage. Water is an excellent non-solvent for the polysulphone family of polymers and also satisfies the requirement of low cost.

Solvents which comply with the above conditions are:

N,N-dimethylacetamide (DMA)
Dimethylsulfoxide (DMSO)
N,N-dimethylformamide (DMF) and
N-methyl-2-pyrrolidone (NMP).

The use of DMA and DMSO as solvent for polymer solution preparation was ruled out due to high cost and health risk. Solutions of PES in DMF were found to be unstable, becoming cloudy on storage or gelling even before the polymer had completely dissolved. The solutions could often be clarified by being heated in a circulating-air oven at temperatures above 65 °C. Upon being cooled, however, most solutions formed a solid gel while others remained stable for indefinite periods. The occurrence of the gelation process was found to be unpredictable at polymer concentration levels above 20%. A similar problem was reported by *Cadotte (1976)* who employed UDEL™ (PSF) as the polymer and DMF as the solvent. Apart from producing unstable solutions, DMF was also considered a health hazard due to its vapours being damaging to the eyes and mucus membranes. It is also known that long exposure of DMF to the skin can cause dermatitis.

Fortunately none of the problems mentioned above is associated with the solvent NMP. It has a high boiling point of 205 °C and a solubility parameter of 11,2 thereby satisfying the two most important requirements. Furthermore solutions of PES in NMP were found to be shelf-stable for indefinite periods *(Tweddle et al., 1983)*. With regard to health considerations, NMP can be taken as being the safest of all the solvents considered above, being only mildly irritating to the skin.

A comparison of solubility parameters and boiling points for the various solvents is given below in condensed tabular form (adapted from *Ventoza and Lloyd, 1985*).

Solvent	δ_d	δ_p	δ_h	δ_t	Boiling point °C
Dimethylformamide (DMF)	8,5	6,7	5,5	12,1	153
N-methyl-2-pyrrolidone (NMP)	8,8	6,0	3,5	11,2	203
Dimethylsulfoxide (DMSO)	9,0	8,0	5,0	13,0	189
N,N-dimethylacetamide (DMA)	8,2	5,6	5,0	11,1	164

3.2.4 ADDITIVES TO CASTING SOLUTION

The procedure to alter membrane performance by adding a third component to a binary solvent/polymer solution, is well known from the literature. The so-called Polymer Assisted Phase Inversion (PAPI) process is discussed by *Kesting (1985)* and will not be described here. Suffice to say that additional components are usually mixed into the casting solution for two main reasons:

(i) to increase the solution viscosity;
(ii) to aid in pore formation during gelation of the membrane skin.

To achieve their purpose, additives must be compatible with the polymer/solvent combination and miscible with the leaching medium. Additives to be used in the casting dope therefore had to be compatible with the PES/NMP mixture as well as be water-miscible.

Binary solutions of polymer and solvent containing a practical percentage of polymer are usually not viscous enough to facilitate easy extrusion of the membrane and bleedthrough of casting solution into the membrane backing material, which will cause the precipitation of membrane polymer in the pores of the backing material during gelation. For this reason polymers and inorganic salts which are compatible with the base polymer, are frequently added to the casting solution.

Additives most frequently mentioned in the literature are organic acids, ketones, inorganic salts and water-soluble polymers such as polyethyleneglycol (PEG) and polyvinylpyrrolidone (PVP). In agreement with *Cabasso (1980)* and *Kesting (1985)*, it was found that PVP and lithium chloride were extremely effective additives for tailoring membrane performance.

3.2.5 MEMBRANE BACKING MATERIAL

It was mentioned previously (section 2.4.1) that the diameters of tubular membranes are usually too large to enable the polymeric membrane to support itself. With hollow fibres, the diameter of the fibre is sufficiently small to form a self-supporting membrane (section 2.4.4).

It is therefore preferable for tubular membranes to be cast on a suitable support material that prevents mechanical damage to the fragile membrane.

This support material must comply with several important requirements:

i) the material must have the ability to be welded ultrasonically or to be joined by other means, to facilitate the formation of a tube from a flat strip;
ii) the material must have adequate strength in tubular form to prevent rupture under operating pressure and temperature;
iii) the material should be porous so as not to restrict permeate flow;
iv) the membrane polymer must adhere to the backing material to prevent delamination of the membrane during use;
v) the material must be resistant to chemical degradation (membrane cleaning solutions) as well as thermal and bacterial degradation so that the excellent stability of the polyethersulphone membrane in these respects can be capitalised upon.

A material which complies with the above requirements is commercially available from the firm Carl Freudenberg of Weinheim, West Germany, under the trade name VILEDON™. A range of VILEDON™ nonwoven fabrics is specifically designed and manufactured for application as support- and drainage layers for semipermeable membranes, such as for ultrafiltration and reverse osmosis.

The material selected for ultrafiltration membrane manufacture was the type FO 2406 consisting of 100% polyester fibres. Carl Freudenberg products are used by membrane manufacturers worldwide.

3.3 INTRODUCTION TO MEMBRANE CHARACTERISATION

Some of the properties which are of special importance in the characterisation of ultrafiltration membranes are listed in TABLE 3.1. The characterisation of membranes is important in order to

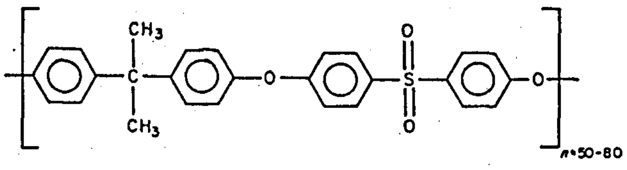
(i) obtain information about the effect of membrane casting parameters on membrane performance,
(ii) to achieve a better understanding of transport mechanisms,
(iii) and as a means of Quality Control.

Unfortunately, no universally employed method for UF membrane characterisation exists in the literature. In the case of RO membranes it has become the norm to specify membrane performance by determining the retention of inorganic solutes at given concentration levels and pressures. The concentrations of these solutes are quantified with relative ease by conductivity measurements. This method is not applicable to UF membranes which do not reject salts or low molecular-mass solutes.

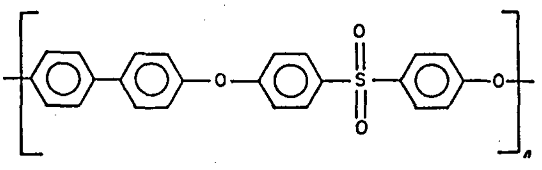
Most manufacturers of UF membranes provide data on permissible pH-, temperature- and pressure ranges as well as pure water flux values and the retention of some macromolecules under defined conditions. Nevertheless it is not possible to predict membrane performance with a complex process stream from this information and such performance has to be quantified by actual tests on the process stream.

FIGURE 3.2
Illustration of the chemical structure of the various polysulphones

UDEL™



RADEL™



VICTREX™

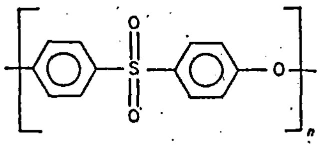


TABLE 3.1 SOME IMPORTANT PROPERTIES OF ULTRAFILTRATION MEMBRANES REQUIRING STANDARDISATION (ADAPTED FROM COTON AND FIFIELD, IN DUTKA, 1981)

PROPERTY	METHOD OF MEASUREMENT	SIGNIFICANCE
Pore-size distribution	bubble point, electron microscopy	most critical property of the membrane filter
Surface pore size	electron microscopy	bacteria cultivation
Retentivity	passage testing	degree of separation
Flow rate	water flow/air flow test	practical filtration
Thickness	thickness guage/ micrometer	affects filter strength and bacteria growth
Strength	microtensile tester	physical stability
Percent porosity	thickness and weight measurement	filter life and flux rate
Solvent resistance	compatibility testing	filter stability
Temperature stability	compatibilty testing	filter life flux rate

3.4 MEMBRANE CHARACTERISATION METHODS

The characterisation of an ultrafiltration membrane can thus be viewed to consist of two distinct approaches:

i) determination of membrane properties for quality control;
ii) determination of membrane performance when subjected to the actual process stream to obtain plant design data.

The most important characteristics which provide information about the performance of the membrane are pore statistics and retentivity.

Pore statistics comprise:

pore size (pore diameter)
pore density (number of pores per unit membrane surface area)
porosity (fraction of membrane volume not occupied by membrane polymer itself)
pore-size distribution (the degree to which the pore size varies across the skin of the membrane)

General methods used for pore size and pore-size distribution determination are:

- i) microscopy
- ii) bubble point technique
- iii) gas permeability data
- iv) pure water flux
- v) porosity
- vi) observed retentivity

Various other methods of membrane characterisation have been reported in the literature *(Smolders and Vugteveen, 1985; Tragardh, 1985)*, which generally make use of asumptions or theories and require specialised apparatus or instrumentation.

3.4.1 MICROSCOPY

Conventional scanning electron microscopy (SEM) cannot be used to detect pores in the surface of an ultrafiltration membrane, since the limit of resolution for this technique is of the same magnitude as typical pore diameters *(Merin and Cheryan, 1980)*. It is, however, a useful tool for studying membrane cross-sections, *i.e.* membrane structure. Inherent weak substructures can be identified with relative ease and casting parameters can be adjusted to provide more desirable membrane substructures.

With the aid of high-resolution SEM, surface porosities of UF membranes can be characterised *(Fane et al., 1981)*.

3.4.2 BUBBLE POINT *(BLASENDRUCK)* TECHNIQUE

One of the first to use this method for determining pore sizes of membranes was Bechhold.

In this method the pressure necessary to blow gas through a water-filled membrane is related to pore size by Cantor's equation:

$$P = \frac{4 \gamma \cos A}{d_p} \qquad (1)$$

where P is the bubble point pressure, γ the surface tension at the gas/liquid interface, A the contact angle between liquid/membrane material and d_p is the pore diameter.

The exact procedure is given in detail in the ASTM Method F316-70 *(1976)*. By soaking the membrane in a liquid with known surface tension and wetting characteristics (contact angle), the pore diameter can be extracted from the equation above by measurement of the pressure at which gas bubbles start to escape from the membrane surface (bubble point). The disadvantage of the method is that it makes use of a theoretical equation which assumes that the pores are right circular cylinders, which is not true in practice. Also the bubble point pressure is really a measure of the diameter of the largest pore since air will pass through the larger pores first.

3.4.3 GAS PERMEABILITY DATA

This method relates pore sizes of polymer membranes based on the gas permeability of porous media. The technique comprises permeability measurements from which the pressure dependence of gas permeability coefficient, K is determined, where

$$K = K_o + \frac{B_o}{\eta} \Delta P \qquad (2)$$

with K_o being the Knudsen permeability coefficient and η the viscosity of the permeate gas, B_o the geometric factor of a membrane and ΔP the mean pressure across the membrane.

The mean pore size of the membrane is calculated from the equation

$$m = \left(\frac{B_o}{K_o}\right) \left(\frac{16}{3}\right) \left(\frac{2RT}{\pi}\right)^{0,5} M^{-0,5} \qquad (3)$$

where M is the molecular mass of the gas. The derivation of equation *(3)* is given in detail by *Yasuda and Tsai (1974)*.

From a plot of gas permeability against mean pressure, K_o can be obtained by extrapolation to zero pressure. Since the above relationship is linear, B_o can be obtained from the slope of the plot. Since all other quantities in equation *(3)* are known, the mean pore size, m can be calculated.

Although the method would seem to be fairly simple, the procedure for obtaining a record of the pressure decay curve can be cumbersome. *Yasuda and Tsai (1974)* proved the validity of equation *(3)* by calculating the mean pore size, m from experiments employing different gases with the same membrane. They found that the parameter B_o and mean pore size m, were independent of the gas used, as equation *(3)* would suggest, provided that the pore size of the support on which the membranes were deposited was much larger than the pore size of the actual membrane. Nevertheless the physical meaning of mean pore size and its absolute value should be interpreted with caution.

A disadvantage of this method is that the membranes have to be dried which results in the deternination of average pore size values lower than actual due to shrinkage of the membrane.

3.4.4 PURE WATER FLUX MEASUREMENT

Intuitively one would expect a good correlation between pore size and water flux through polymeric membranes, as they are finely porous structures. In their simplest form, a membrane can be viewed as a thin film with pores consisting of right-angled circular cylinders of uniform diameter extending through the entire thickness of the film at right angles to the surface.

On the basis of this assumption the water flux through a membrane and the pore size are related by the Hagen-Poiseuille model:

$$J = \frac{\epsilon \; d_p^{\,2} \; \Delta P_T}{32 \; \Delta x \; \eta} \qquad (4)$$

where

J = flux per unit area of membrane
ϵ = porosity
ΔP_T = applied pressure
η = viscocity of the solvent
Δx = membrane thickness
d_p = pore diameter

With a knowledge of the membrane thickness and porosity, pore size can be obtained from equation *(4)* by performing a simple flux measurement.

Due to the simplicity of this method it is frequently used to correlate pore sizes of actual membranes, especially since the water flux also provides a practical measure of performance.

3.4.5 POROSITY

The porosity of a membrane can be viewed as the fraction of volume not occupied by membrane polymer, or so-called void volume.

Porosity is related to pore size by *(Cheryan, 1986)*

$$\epsilon = N \; (\pi/4) \; d_p^{\,2} \qquad (5)$$

where

N = number of pores per unit area
d_p = pore diameter

In practical terms the porosity can be regarded as the volume of water occupying the membrane pores. This volume is easily determined by simple gravimetric means from the difference between the wet and dry mass of the membrane. The void volume is then calculated from this difference and the density of the void-free polymer.

3.4.6 OBSERVED RETENTIVITY

The only practical means of measuring the selectivity of a membrane is a filtration test in which a solution of a well characterised solute is filtered with the membrane under defined conditions. The observed retention of the particular solute is then calculated from

$$R_{obs} = 1 - (C_p/C_r) \qquad (6)$$

where

C_p = concentration of solute in permeate
C_r = concentration of solute in retentate

Requirements to which solutes for use in filtration tests should comply to are that the substance should not adsorb onto the membrane, have a narrow molecular mass distribution and be stable in solution. Water soluble polymers such as dextrans, polyethylene glycol (PEG), polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP) and bovine serum albumin (BSA) are widely used for this purpose.

Most manufacturers of ultrafiltration membranes indicate a cut-off value for a specific membrane when it is tested with a polymer or protein of known molecular mass. Unfortunately at present no standard of solutes or test conditions exist for the filtration test. Also the molecular mass cut-off (MMCO) of a membrane refers to an arbitrarily selected figure of retention, of a solute with a specific molecular mass, that would seem to vary between 80 and 95% on the retention scale from manufacturer to manufacturer. A direct comparison between performance of membranes from various suppliers based on their specification is therefore impossible since different methods and definitions are employed.

3.4.6.1 *Factors affecting the retentivity*

The problem of membrane selection is compounded by the fact that the results obtained from observed retentivity measurements can not be extrapolated directly to predict membrane performance associated with complex process streams. Solute/solute and solute/membrane interactions, concentration polarisation and fouling phenomena can change the separation characteristics of membranes dramatically. The retentivity of UF membranes is affected by the following factors:

Size of the solute molecule: Larger molecules will be retained more easily than smaller ones will. Furthermore, actual solute molecules do not have a fixed size, but show a molecular mass (size) distribution about a mean value.

Shape of the solute molecule: Globular molecules are retained more easily than linear molecules of the same molecular mass are since linear molecules can be deformed forced through the pores in the membrane skin *(Nguyen and Neel, 1983 a)*.

Nature of Solute: The retentivity can be influenced by the adsorbtion of solute to the membrane or by degradation (instability) of the solute in solution.

Nature of Solvent: The nature of the solvent can drastically alter the retentivity of a membrane with regard to a particular solute. Polyvinylpyrrolidone was retained to greater extent when it was in alcoholic solvents than when it was in water, whereas the opposite was noted for polyethyleneglycol, due to the difference in solvation of the two polymers by these solvents *(Nguyen and Neel, 1983 b)*.

Presence of other solutes: Molecules can interact with one another to cause molecular changes. More important, however, is the hindrance of molecules of similar size due to solute-solute and solute-membrane interactions, which result in retention different from that if they had been present individually *(Porter, 1979)*.

Experimental conditions: A change in experimental operating conditions will lead to a change in the degree of concentration polarisation, which will influence the retention of the particular solute *(Nakao and Kimura, 1981)*.

3.4.6.2 *Determination of molecular mass cut-off curves*

The observed retention is usually plotted against the molecular mass of the particular molecule used in the experiment. Determination of the complete cut-off curve for a particular ultrafiltration membrane requires the use of about six different solutes. The method for the determination of cut-off curves is discussed in detail in the literature *(Capannelli et al., 1983* and *Jonsson, 1985)*.

The major draw-back of the method is that the solute concentration in the permeate and bulk streams is neither quickly nor accurately determined. Various methods have been suggested, among them gel-permeation chromatography *(Cherkasov et al., 1981)*, differential refractometry *(Schwarz et al., 1982)* and spectrophotometry *(Nakao and Kimura, 1981)*.

The real practical value (in terms of the retention characteristics of ultrafiltration membranes with real process streams) of experimentally determined molecular mass cut-off curves is therefore questionable *(Tragardh and Olund, 1986)* due to the many factors which affect the retentivity (section 3.4.6.1). Consequently the author made no effort to construct molecular mass cut-off curves for various membrane types.

CHAPTER FOUR

MEMBRANE MANUFACTURING EQUIPMENT AND MEMBRANE FABRICATION

4.1 TUBE-WINDING EQUIPMENT

The tubular UF membrane consists of two main constituents *i.e.* the polyethersulphone membrane and the polyester support fabric. In order to obtain the tubular configuration, a flat strip of non-woven polyester support fabric has to be transformed into a tube. This is achieved by winding the strip of fabric around a mandrel in a helical fashion and fusing the overlapping edges ultrasonically to form a continuous tube. The principle is illustrated in FIGURE 4.1.

The equipment used to fabricate tubular ultrafiltration membranes by the wet phase-inversion process, is described in subsequent paragraphs.

4.1.1 TUBE-WINDING MACHINE (TWM)

The tube-winding machine permits the production of tubular UF membranes by simultaneous fabrication of the support tube and extrusion of a membrane casting solution film on the inside of the support tube. The same mandrel which is used for the winding of the support tube, also serves as an extrusion device for the casting solution which forms the membrane *(Jacobs, 1980)* and is illustrated in FIGURE 4.2.

Polymer solution from a feed hopper is fed down the hollow centre of the mandrel with the aid of a precision gear pump. The mandrel has a narrow section between the upper shaft, around which the support tube is formed, and the lower extrusion die section. Casting solution is applied to the inside of the support tube through four orifices in the narrow section of the mandrel. The difference in diameters between the mandrel shaft and extrusion die is typically 0,4 mm. Membrane thickness prior to gelation is thus theoretically 0,2 mm. A schematic diagram of a mandrel used for the production of UF membranes is shown in FIGURE 4.2.

Fabric is fed continuously from a feed roller along a guide roller system to the mandrel (FIGURE 4.3). A driving belt, the angle of incidence, tension and speed of which can be adjusted, ensures the smooth helical winding of the fabric strip around the mandrel. By adjusting the angle of incidence of the driving belt to the mandrel, the amount of overlap between the edges of the wound tube can be altered so as to form a weld-seam of adequate strength (FIGURE 4.4).

The fabric feed rate and casting solution feed rate are controlled to keep a constant level of casting solution in the annulus of the support tube and mandrel, halfway between the bottom of the mandrel shaft and the top of the extrusion die to maintain a constant extrusion pressure. The tube winding/extrusion mandrel is situated directly above a coagulation tank in which the membranes are immersed to cause gelation and coagulation of the casting solution (FIGURE 4.5). Tube production, membrane extrusion and gelation are thus accomplished in a single continuous process.

The tube-winding machine, together with all supporting equipment, is enclosed in a temperature-controlled room (FIGURE 4.6).

4.1.2 ULTRASONIC WELDER

The apparatus used to fuse the overlapping edges of the fabric strip to transform it into a support tube, is manufactured by RINCO ULTRASONICS, Switzerland. The device consists of three main components, *i.e.* power supply, converter and welding horn.

The power supply of the unit used is designed to deliver an output of exactly 35 kHz frequency. A tuner allows operation within a range of 200 Hz, however, resulting in a lower power output.

The sonic converter can be regarded as the heart of the ultrasonic welding system and it is this component that converts the 35 kHz electrical energy supplied by the power source to mechanical energy by a phenomenon known as the piezoelectric effect.

The horn is a 0,5 wave length resonant metal section tuned to vibrate at exactly 35 kHz, thereby transmitting vibratory energy to the work-piece.

The degree of fusion between the overlapping fabric edges is controlled by varying the pressure applied by the horn to the fabric. The amount of pressure required to obtain good fusion is dependent on the welding speed, fabric characteristics and width of overlap of the fabric edges. Increase in horn-pressure leads to better fusion and *vice versa*. Excessive horn-pressure on the fabric however, results in the excessive melting of the fabric at the contact point, causing a cutting, rather than a welding, action.

4.1.3 CASTING SOLUTION FEED PUMP

Casting solution is fed from a feed hopper to the extrusion mandrel by a precision gear pump. The pump is supplied by BARMAG, West Germany, and has a volumetric feed rate of 1,2 $m\ell$ per revolution. Speed control is achieved with a KOPP ball series variator that allows stepless variation of 1/3 to 3 times input speed. A reduction gear box between the variator output and pump drive shaft, lowers pump speed by a ratio of 50 : 1 (FIGURE 4.7). With a motor speed of 900 min^{-1}, this system allows a feed rate variation from 7,2 $m\ell$ per minute to 64,8 $m\ell$ per minute, making it extremely flexible in terms of operation.

4.1.4 COAGULATION TANK

The coagulation tank is made from a 240 mm diameter 4 m long PVC pipe with a flange at the bottom to facilitate cleaning of the inside of the tank. The tank is supported in the vertical position and filled from the bottom. An overflow is provided at the top of the tank to allow for continuous supply and circulation of fresh non-solvent during membrane manufacture.

The coagulation tank stands free of other supporting structures of the TWM to avoid the transmission of vibration from drives and pumps. Vibration causes non-solvent liquid level disturbance in the coagulation tank, which leads to the formation of unwanted precipitation lines on the membrane surface and thus an inferior product.

4.1.5 AUXILIARY EQUIPMENT

Additional equipment required for membrane production furthermore includes:

i) small RO unit (FIGURE 4.8) for pure-water production (non-solvent for membrane precipitation);
ii) facility to control temperature of coagulation tank contents;
iii) casting room temperature control;
iv) coagulation tank and casting room temperature indicators;
v) digital timer to enable production of equal tube lengths;
vi) mixer for casting solution preparation.

FIGURE 4.1

Illustration showing the tube-winding principle. A fabric strip is wound around a mandril in a helical fashion and transformed into a tube by fusion of the overlapping edges with an ultrasonic welding device.

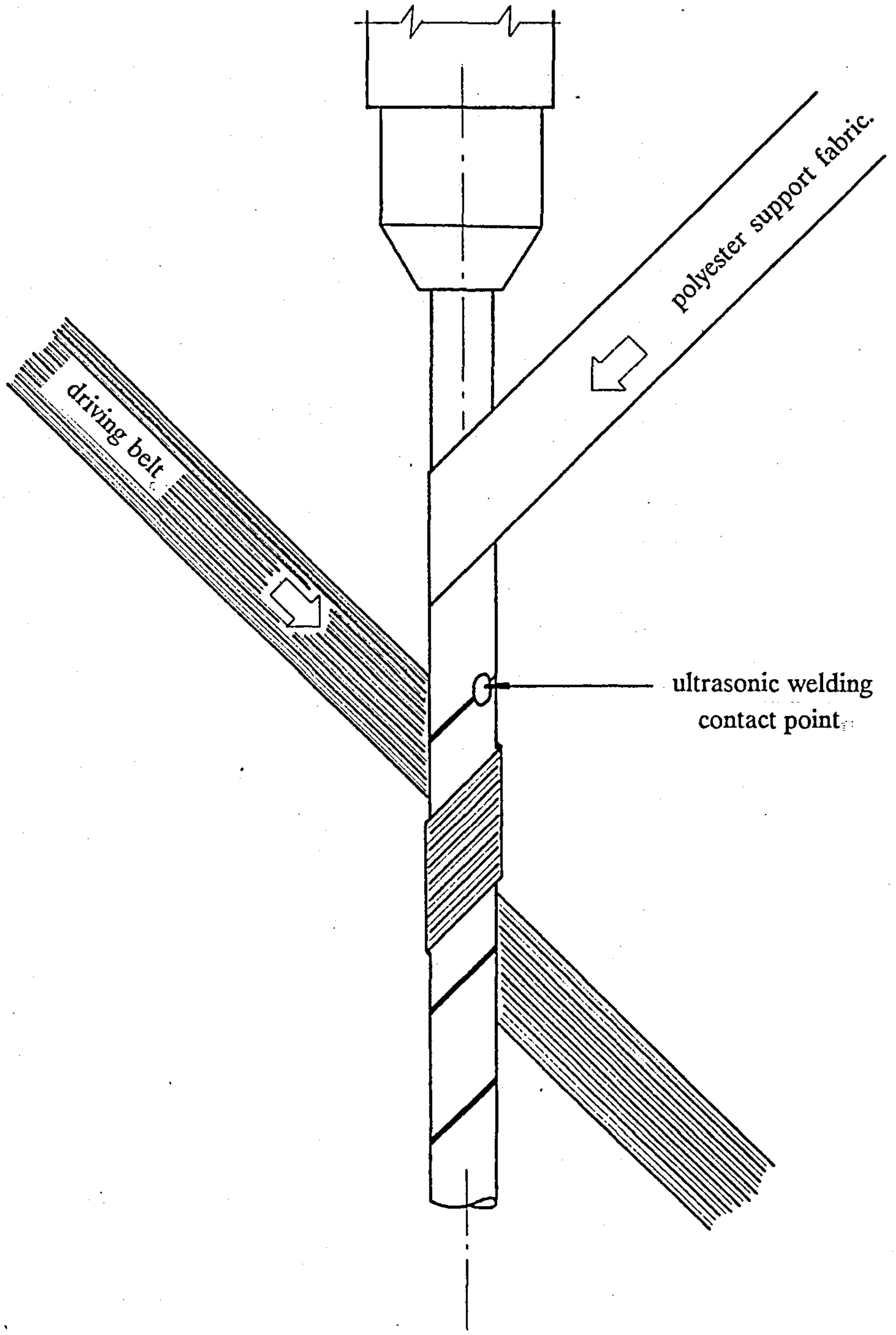


FIGURE 4.2
Schematic of a mandril used for tubular ultrafiltration membrane manufacture

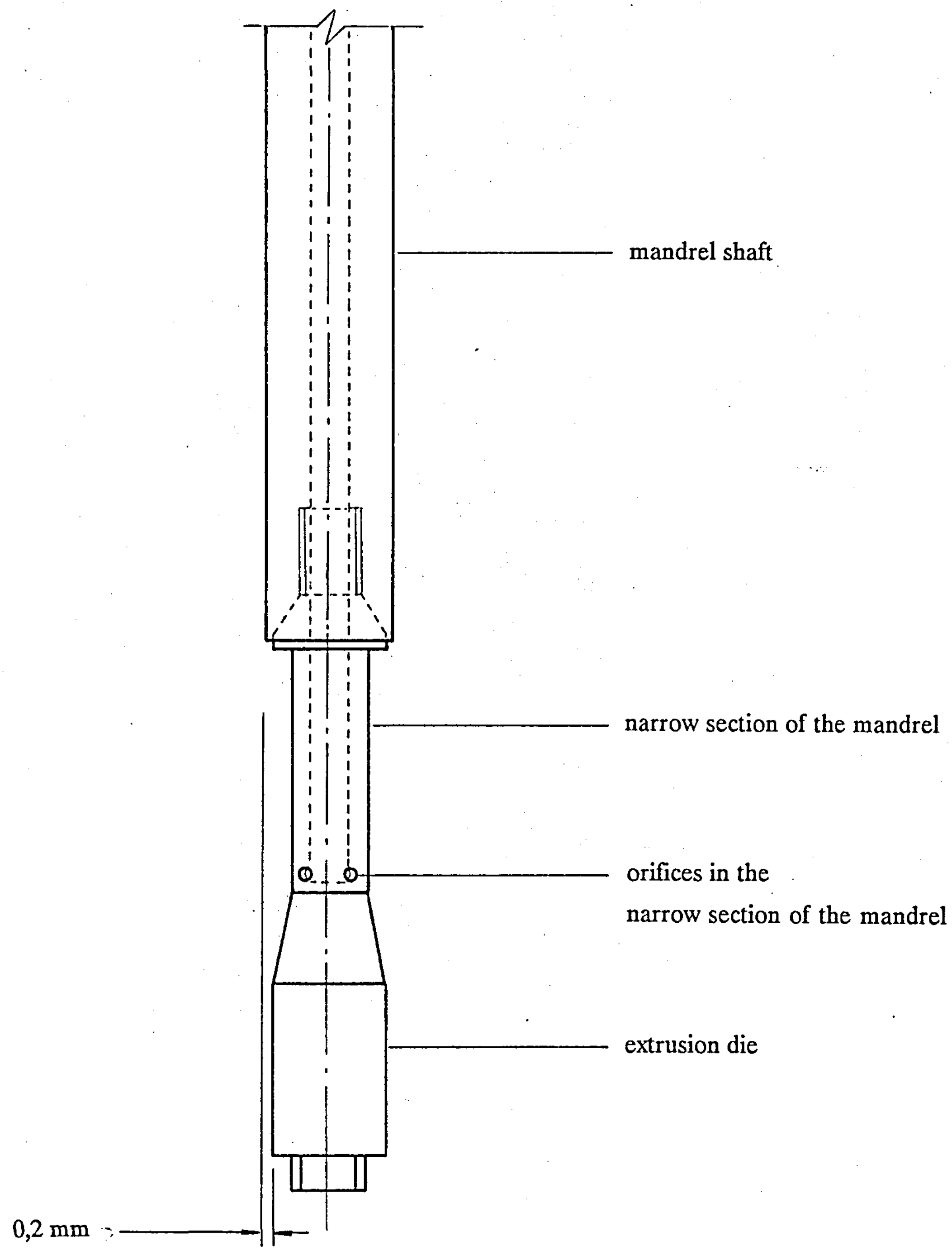


FIGURE 4.3
Photograph of fabric feed and guide roller system

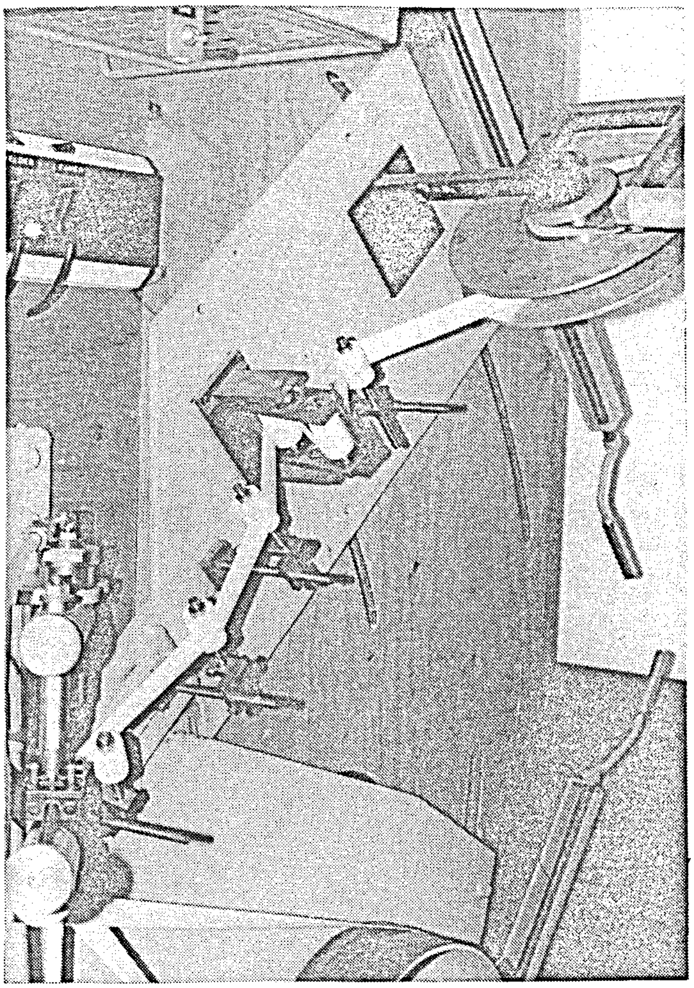


FIGURE 4.4
Photograph showing general tube-winding machine arrangement

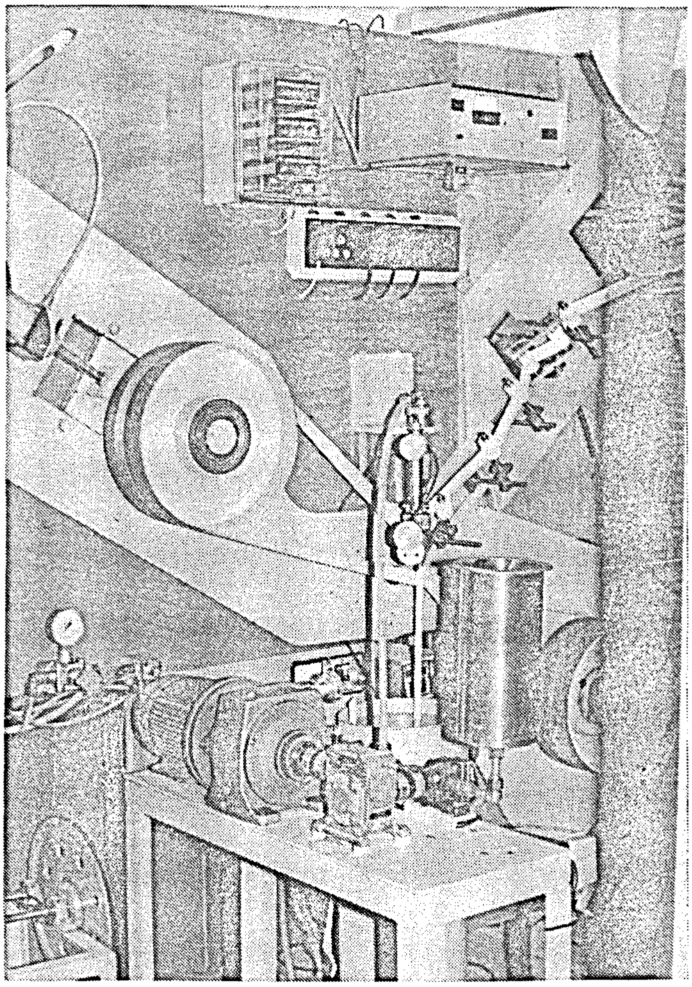


FIGURE 4.5
Photograph of the heart of the tube-winding machine with coagulation tank

Close-up view of the tube-winding procedure with the ultrasonic welder shown at the left and the coagulation tank at the bottom of the picture.

FIGURE 4.6
Photograph of tube-winding machine enclosure

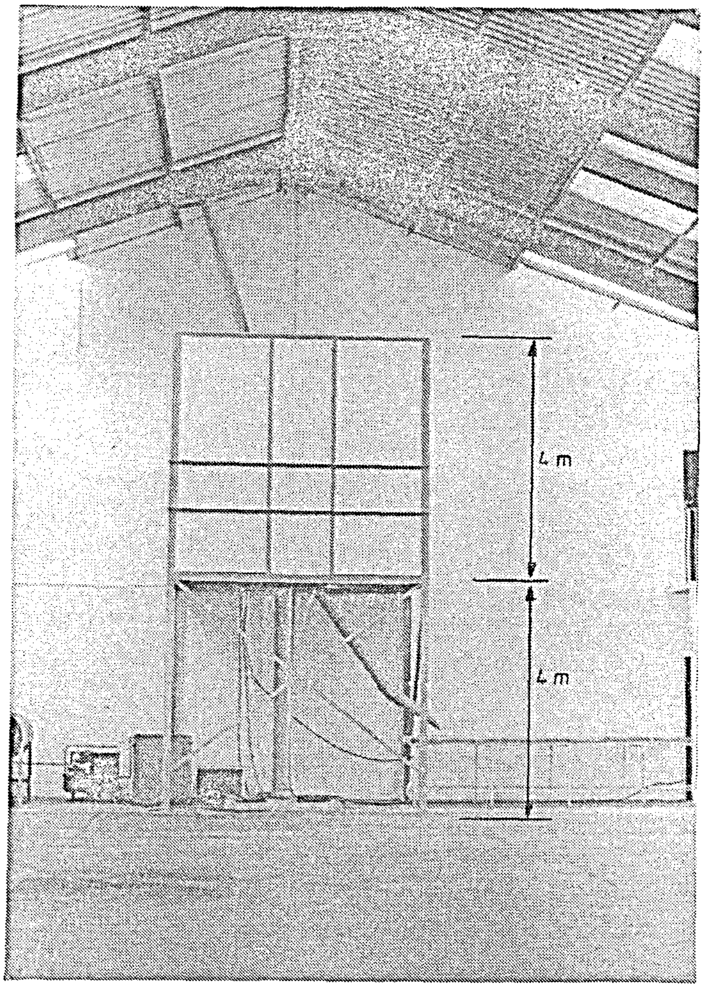


FIGURE 4.7

Photograph of casting solution feed system

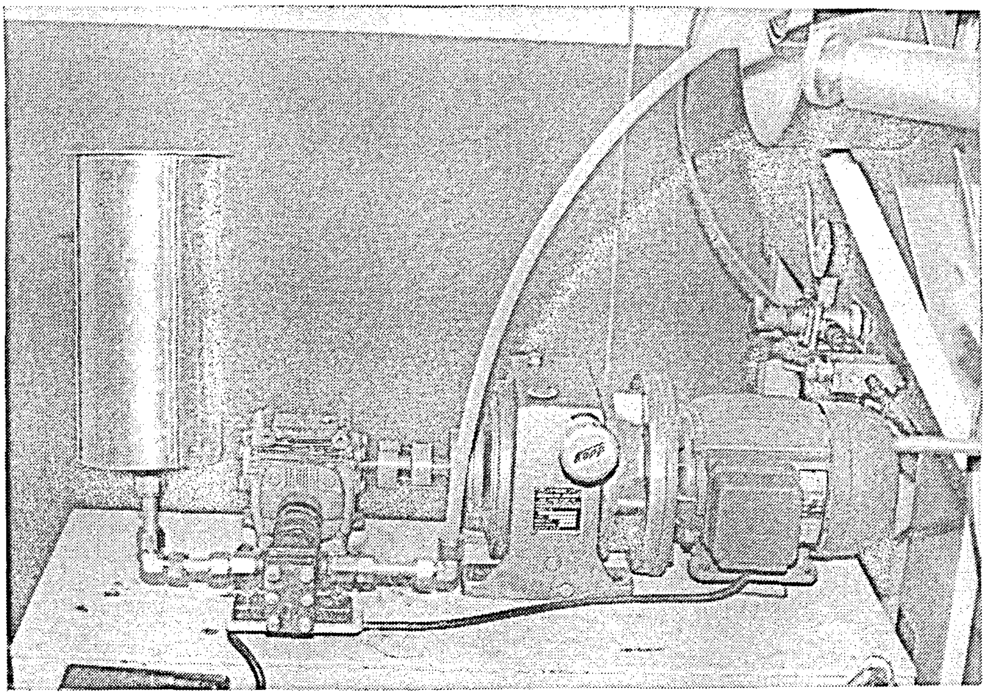
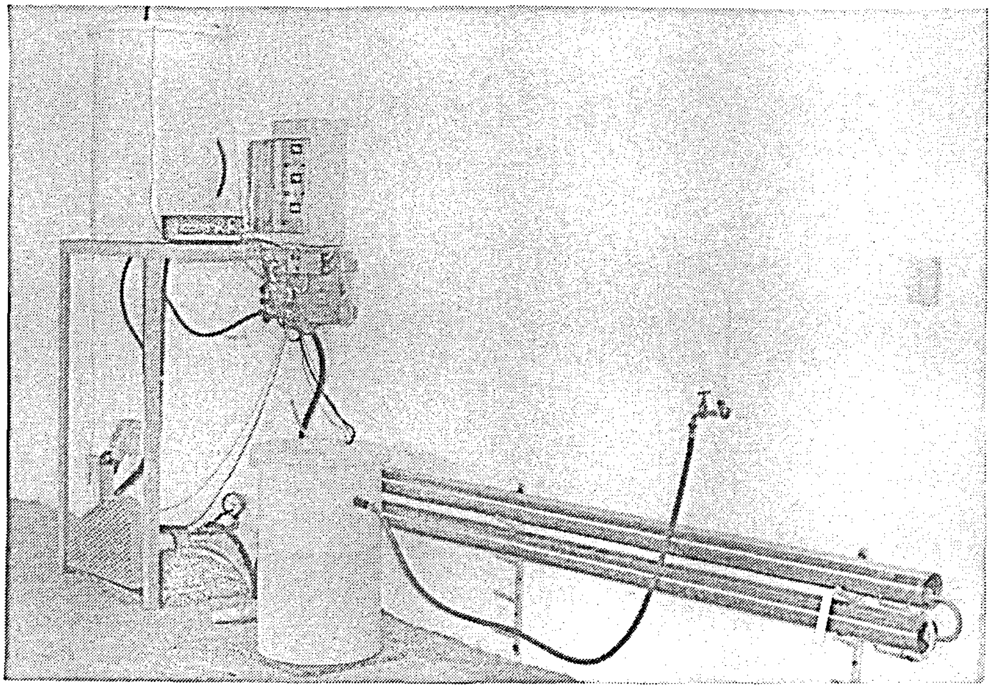


FIGURE 4.8

Photograph of the 2,4 $m^3 day^{-1}$ RO plant for pure water production from tap water (ROTAP) used in the manufacture of UF membranes.



4.2 MEMBRANE MANUFACTURE

The production of tubular UF membranes by the phase-inversion method, is a three-step process consisting of casting solution preparation, tube/membrane manufacture, membrane leaching and ultimately storage of completed tubular membranes.

4.2.1 CASTING SOLUTION PREPARATION

The simplest casting solution for the manufacture of membranes consists of a polymer dissolved in a suitable solvent, *i.e.* a binary solution. Variation of membrane structure and pore size is limited when binary solutions are employed. All casting solutions used in this work contained polymer, solvent and one or more additives. In some solutions a mixture of solvents was used.

Casting solutions were prepared by weighing off the correct amount of polymer and additive into a dry, clean glass container to which solvent was added. With highly viscous solutions, *e.g.* with the addition of PVP and $LiC\ell$, it is advantageous to first completely dissolve the modifiers and then to add the correct amount of base polymer.

The tightly stoppered glass containers were then placed on a roller mixer which rotated the containers at 6 min^{-1}, until a homogenous solution was obtained. Depending on room temperature, solution composition and viscosity, the duration of this process varied from 24 to 72 hours. The entire process can be speeded up by heating the container to not more than 60 °C in a convection oven without affecting the nature of the casting solution.

4.2.2 TUBE AND MEMBRANE PRODUCTION

The support tube and membrane are manufactured in a single operation as described earlier. Fabric feed speed and casting solution feed rate are adjusted until the liquid level in the annulus between the support tube and narrow neck section of the mandrel remains constant. Immediately after extrusion, the tubes are immersed in the gelation bath to precipitate the polymer matrix. The film consists of a thin, dense skin which is supported by a thicker, porous substructure which is integral with the support tube. The mechanism of the process is described in detail by *Cabasso (1980)*, *Kesting (1985)* and *Strathmann (1985)* and will not be repeated here.

Casting-atmosphere conditions were maintained at 20 to 25 °C and approximately 60% relative humidity. Coagulation-bath temperature was usually controlled at 20 °C to an accuracy of 1 °C. In order to obtain reproducibility of consecutive, identical membrane batches, the casting-atmosphere conditions and especially the coagulation-bath temperature, must be carefully controlled and kept constant if repeatability of performance between similar membrane batches is desired. Variation in coagulation-bath temperature has a marked effect on membrane structure and performance, even when casting solutions of identical composition are used *(Jacobs, 1988)*.

During casting of the membrane, the coagulation tank is supplied with fresh non-solvent (ROTAP) to keep the concentration of solvent (leaching from the polymer solution) in the tank at a low level. The non-solvent used in the coagulation tank was ROTAP with or without the addition of surfactants, inorganic salts or solvent.

Addition of surfactants such as sodium lauryl sulphate (SLS) or Triton X-100 (sodium dodecyl sulphate) to the coagulation tank in small concentrations (10 to 50 ppm), aid in the formation of a very smooth membrane skin. The presence of inorganic salts in the coagulation tank tends to slow down the precipitation process, leading to denser, more uniform membrane structures *(Jacobs, 1988)*. A similar effect can be achieved by lowering the coagulation tank temperature. Membranes prepared in this way are generally associated with a lower pure water flux value. The addition of solvent to the coagulation tank, on the other hand, resulted in membranes with higher flux values. The effect of solvent concentration in the coagulation tank on membrane performance is given in section 5.6.

4.3 LEACHING OF MEMBRANES

After extrusion, coagulation and gelation of the nascent membrane, a leaching step is required to remove excess solvent trapped in the membrane substructure.

Immediately after formation of the membrane skin, the exchange between solvent and non-solvent is greatly reduced, since the membrane skin acts as a barrier to fluid transport. Although the membranes are gelled almost instantly on contact with the non-solvent in the gelation bath, they are given a 30-minute leaching period in ROTAP to allow complete phase separation which fix the matrix morphology.

4.4 MEMBRANE STORAGE

Because of the excellent resistance to microbial degradation of polyethersulphone membranes, no preservation chemicals are required once the membranes have been manufactured. The membranes should, however, be stored wet to prevent excessive shrinking which results in loss of permeability. Membranes should be rinsed with good quality water, containing some formaldehyde to prevent the formation of slime when stored in a sealed container. Alternatively, the tubular membranes were stored in a flat bottomed, rectangular tank which was supplied on a continuous basis with fresh reverse osmosis permeate derived from tap water (ROTAP). The effect of storage on membrane performance is discussed in section 5.4.

CHAPTER FIVE

MEMBRANE EVALUATION

5.1 PURE WATER FLUX TEST

One of the easiest, practical methods for obtaining an indications of membrane pore size, is by physical measurement of the pure water flux through a membrane at controlled conditions. It follows from equation *(4)* in section 3.4.4 that the measured water flux gives a direct indication of pore size. Therefore in order to check the repeatability of membrane integrity from batch to batch, the measured pure water flux can provide first-order information in this regard.

The quality of data obtained through pure water flux tests is strongly dependent on the quality of water used as solute in this experiment. The quality of this water should remain practically constant from one test to another so as not to cloud the resultant data through excessive deviation about the mean. This was achieved by using reverse osmosis permeate obtained from tap water as feed source, or so called ROTAP.

The water flux was measured by selecting six random tubes from a production batch of 40 tubes. The selected tubes were then inserted into perforated stainless steel tubes of similar internal diameter, each 1 m long. Flux was then measured on each individual tube at the conditions given in TABLE 5.1.

TABLE 5.1 TEST CONDITIONS FOR PURE WATER FLUX MEASUREMENTS

Solute	ROTAP
Feed pressure	100 kPa (after pre-pressurisation for 10 minutes at 600 kPa)
Linear velocity	$1\ m\ s^{-1}$
Feed temperature	20 °C
Pure water flux	As determined experimentally for particular membrane type.

A mean value was then computed from the six individual results. The effect of the various operating parameters on pure water flux for the 719 membrane type are shown in FIGURES 5.1 to 5.2.

Linear relationships between feed temperature, feed pressure and flux were obtained with an increase in pressure and temperature resulting in a corresponding increase in flux, as expected *(Nguyen et al., 1979)*.

The slope of the temperature/flux curve (FIGURE 5.1) showed a value of 22 $\ell m^{-2}h^{-1}$ per degree temperature increase. Flux increase was found to be 4 $\ell m^{-2}h^{-1}$ per pressure unit (kPa) increase (from data illustrated in FIGURE 5.2).

After the pure water flux test, a feed solution of ROTAP and Congo Red dye was used to facilitate the detection of membrane imperfections. Identical conditions to the ones used in the pure water flux test were used, utilising the same membranes. After the dye test, each membrane tube was inspected for pin holes and other imperfections which were highlighted by uptake of dye on the membrane surface.

In the event of dye passage through the membrane or other imperfections, the particular membrane batch was scrutinised more closely and rejected if necessary, rather than being used in the production of modules. The failure of such modules in a later Quality Assurance test and subsequent loss of construction material was prevented in this manner.

The dye concentration in the feed solution had a marked effect on the flux rate through the membrane *(Cooper, 1982)*. The curve for the relationship between the water flux rate and the dye concentration for the 719 membrane is shown in FIGURE 5.3.

FIGURE 5.1

Effect of feed temperature on pure water flux

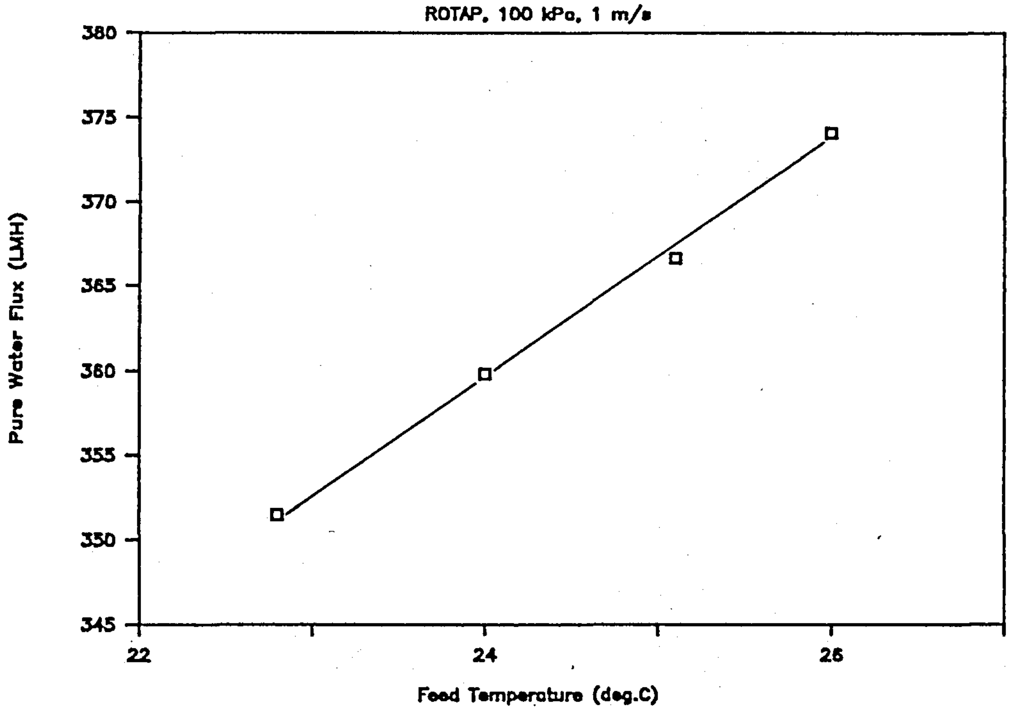


FIGURE 5.2

Effect of feed pressure on pure water flux

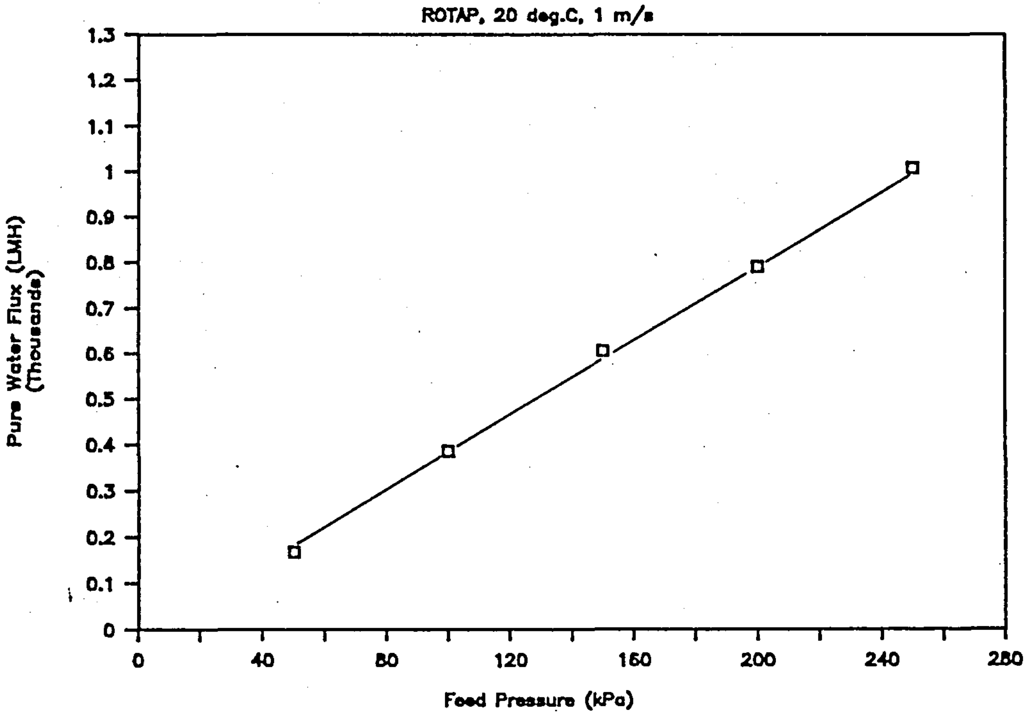
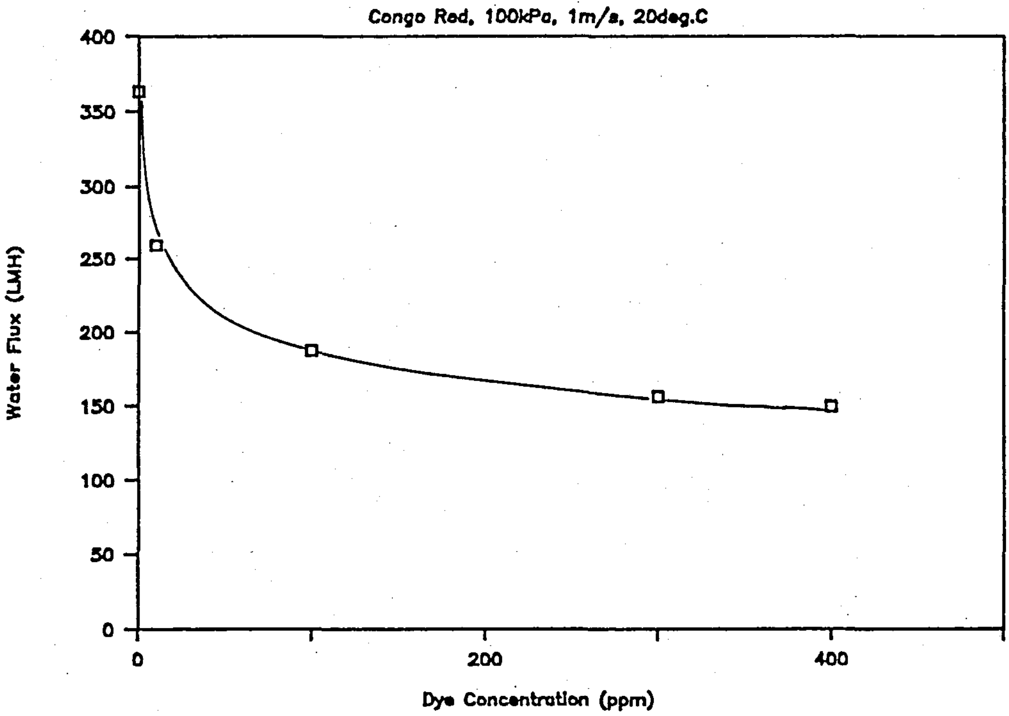


FIGURE 5.3
Pure water flux *vs*. dye concentration



The curve followed an exponential decline of the form:

$$J = a \exp (b \cdot \text{dye concentration})$$

with $R^2 = 1,0$
a = 366 $\ell m^{-2}h^{-1}$
b = -0,149 $\ell m^{-2}h^{-1}$ per ppm.

An asymptote of approximately 150 $\ell m^{-2}h^{-1}$ at a dye concentration of 400 ppm is reached. Flux is relatively independent of dye concentration at values above 400 ppm, implying that simultaneous flux and dye tests could be performed at concentrations above 500 ppm. Unfortunately, at these concentrations the colour of the membrane surface was intense, making it impossible to distinguish fine imperfections in the membrane. Routine dye tests were therefore performed after a pure water flux test at dye concentrations of about 50 ppm.

5.2 RETENTION TEST

Physical retention measurements are the only practical means, besides actual studies using process streams, of determining membrane performance.

The test comprises performing filtration tests using the particular membrane of interest and solutions of defined macro-molecules at specified conditions. Differential refractometry was ruled out as a method for determining the concentration of PVP/water solutions used in the characterisation of membranes. This was because in the concentration range used, the solutions showed a variance only in the third decimal of the refractive index.

Spectrophotometry was also investigated as a possible means for measuring the concentration of PVP/water solutions. Although PVP shows an absorbance peak at 215 nm, no correlation between absorbance and PVP concentration could be established.

Ultimately it was decided to determine the concentration of PVP solutions gravimetrically. Despite being tedious and unsophisticated, the method provided data of reasonable accuracy.

Filtration test using PVP as solute were performed under the conditions shown in TABLE 5.2.

TABLE 5.2 TEST CONDITIONS FOR RETENTION TEST WITH PVP SOLUTIONS

Feed pressure	500	kPa
Feed temperature	20	°C
Linear flow velocity	1	m s^{-1}
Solute concentration	5	g ℓ^{-1}
Test duration	0,25	hours

To limit the effect of concentration polarisation, the velocity was selected so as to operate in the turbulent region, while keeping solute concentration low (0,5%). Duration of the test was reduced to 15 minutes to minimise the effect of fouling, but to provide enough time for the stabilisation of operating conditions.

When sample values of 50 mℓ were used and the sample mass was determined to an accuracy of four decimals, the maximum error was about 10% when it was assumed that a discrepancy occurred in the third decimal. The absolute error increased with an increase in retention and varied from about 2% at the 80% retention level to 8% at the 95% retention level.

For all practical purposes the accuracy of the method was considered to be adequate at the levels and sample volumes mentioned above.

The real practical value of experimentally determined molecular mass cut-off curves is therefore questionable *(Tragardh and Olund, 1986)*. Consequently no effort was made to construct the cut-off curves for various membrane types.

In order to obtain an indication of the retention characteristics of ultrafiltration membranes, single filtration tests were carried out, using solutions of PVP (polyvinylpyrrolidone) at the controlled conditions stated previously.

Typical retention values for the different membrane types are given in TABLE 5.3. The particular membrane type that showed good performance was the 719 type and this particular membrane was used extensively in bench and pilot studies.

TABLE 5.3 TYPICAL MEMBRANE PERFORMANCE DATA OBTAINED FROM STANDARD PURE WATER FLUX AND RETENTION TESTS

Membrane type	**308**	**309**	**713**	**719**
Pure water flux ($\ell m^{-2}h^{-1}$)	960	190	670	380
PVP 40 000 MM				
Retention (%)	75	99	83	
Flux ($\ell m^{-2}h^{-1}$)	51	35	44	
PVP 24 000 MM				
Retention (%)		29	4	70
Flux ($\ell m^{-2}h^{-1}$)		93	158	60

5.3 EFFECT OF POLYMER CONCENTRATION AND PRESENCE OF ADDITIVES IN CASTING SOLUTION ON MEMBRANE PERFORMANCE

A substantial amount of work has been done to investigate the effects on membrane performance of the various additives used in the preparation of casting solutions employing polysulphone, either UDEL™ or RADEL™ *(Nishimura, 1977).*

The objective of this cursory investigation was to determine whether the same trends are evident when polyethersulphone (VICTREX™ 4800G) is used. As such it must be emphasized that the experiment was not structured to result in the manufacture of a membrane with optimum performance.

The effects of polymer concentration, at two levels, and additives at fixed concentration levels, on membrane performance, were investigated. The concentration of polyethersulphone (PES) in the casting solution was fixed at either 14 or 18 mass % and N-methyl-2-pyrrolidone (NMP) was used as solvent. The additives used were polyethyleneglycol (PEG) of 400 MM at 2 mass %, polyvinylpyrrolidone (PVP) of 40 000 MM at 5 mass % and anhydrous LiCℓ at 0,2 mass %.

It is known that both PVP and PEG act as pore formers, and that PVP serves to increase the solution viscosity as well. These polymers are compatible with PES and form a homogenous solution. Upon gelation these polymers are entrapped in the PES-rich and PES-poor regions. After gelation these polymers are leached out of the membrane structure and are replaced by water with resultant polymer matrix formation *(Cabasso, 1980).*

The inorganic salt lithium chloride, on the other hand, serves to increase casting solution viscosity. The possibility that the metal part of the salt forms a physiochemical bond with the polyethersulphone molecules, is not excluded. This would explain the sharp increase in casting solution viscosity and improvement in membrane retention characteristics even when the salt is present at very low concentrations.

The membrane manufacturing procedure and casting conditions were kept constant throughout the experiment. Random samples were drawn from each batch and these membrane samples were tested by means of the standard methods.

5.3.1 POLYMER CONCENTRATION

An increase in polymer concentration in the casting solution resulted in an increase in solute rejection and a decrease in flux, provided all other parameters were kept constant. These findings are in accordance with the findings of *Tweddle (1983)*.

This fact is borne out when samples 1 and 2 in TABLE 5.4 are compared. The same tendency was evident when either LiCℓ or PVP were added to the solution (see samples 3, 4 and 5, 6). When PEG was added to the casting solution, the direct opposite effect was observed (samples 7, 8). It was found during earlier studies that these additives at concentration levels higher than those used in this experiment tended to cause gross imperfections in membrane structure.

5.3.2 ADDITION OF PVP

At constant PES concentration, the addition of PVP to the casting solution resulted in a membrane with higher rejection and decreased flux *(Tweddle, 1983)*. However at the upper PES concentration level the decrease in flux was not as pronounced as at the lower level. The same held true for the gain in rejection with the addition of PVP as shown by samples 1 and 5 as well as 2 and 6.

5.3.3 ADDITION OF LiCℓ

The effect of LiCℓ on membrane performance is essentially identical to that of PVP. Lower concentration levels were required to achieve the same or even greater increase in rejection by the membrane. This can be attributed with relative certainty to the difference in interaction mechanisms between PES and PVP on one hand and PES and LiCℓ on the other. While PVP acts primarily as a pore former, LiCℓ has the ability to form a physiochemical bond with PES itself by a mechanism which is still unclear. This results in a modified polymer matrix giving increased rejection characteristics due to a higher precipitation rate of the polymer during the immersion step. This phenomenon is due to the lower thermodynamic stability of the casting solution arising from the macromolecular interactions because of the presence of LiCℓ as well as the high tendency of the additive to mix with water *(Bottino et al., 1988)*.

5.3.4 ADDITION OF PEG

The addition of PEG 400 seems to have an overall detrimental effect on retention whereas it usually increases flux. The same effect was noticed even when PEG 400 was used in combination with other additives. Similar results are reported by *Uragami et al. (1981)* who used PVDF and NMP dopes.

5.3.5 COMBINATION OF ADDITIVES

The addition of either PVP or LiCℓ to the binary casting solution resulted in increasing membrane retention and decreasing membrane flux, with LiCℓ having the stronger effect. When these components were combined, however, the overall effect was not as pronounced and an intermediate value was attained (compare the results for samples 2, 4, 6 and 13 which are illustrated in FIGURE 5.4).

Addition of PEG 400, on the other hand, resulted in a lowering of retention and increase in flux at the 18% PES concentration level (compare samples 2 and 8). When PEG was used in combination with LiCℓ, a larger increase in retention resulted then when it was combined with PVP, again illustrating the effectiveness of LiCℓ (compare samples 8, 10 and 11).

LiCℓ therefore seems to have a strong positive effect on membrane retention when present on its own or in combination with PVP, despite the negative effect of PEG. The same holds for the addition of PVP, although the effect is not as strong.

When analysing the results for the various other combinations it follows that the presence of PEG always had a detrimental effect on retention and resulted in an increase in flux values.

5.3.6 CONCLUSIONS

It can be concluded that the addition of PVP and LiCℓ to the casting solution at the concentration levels used in this experiment resulted in an increase in retention while flux values did not vary to a great extent. The use of PEG 400 in the casting solution led to a decrease in retention by the resultant membrane but could possibly be used in combination with PVP and LiCℓ to improve flux values while maintaining similar retention characteristics.

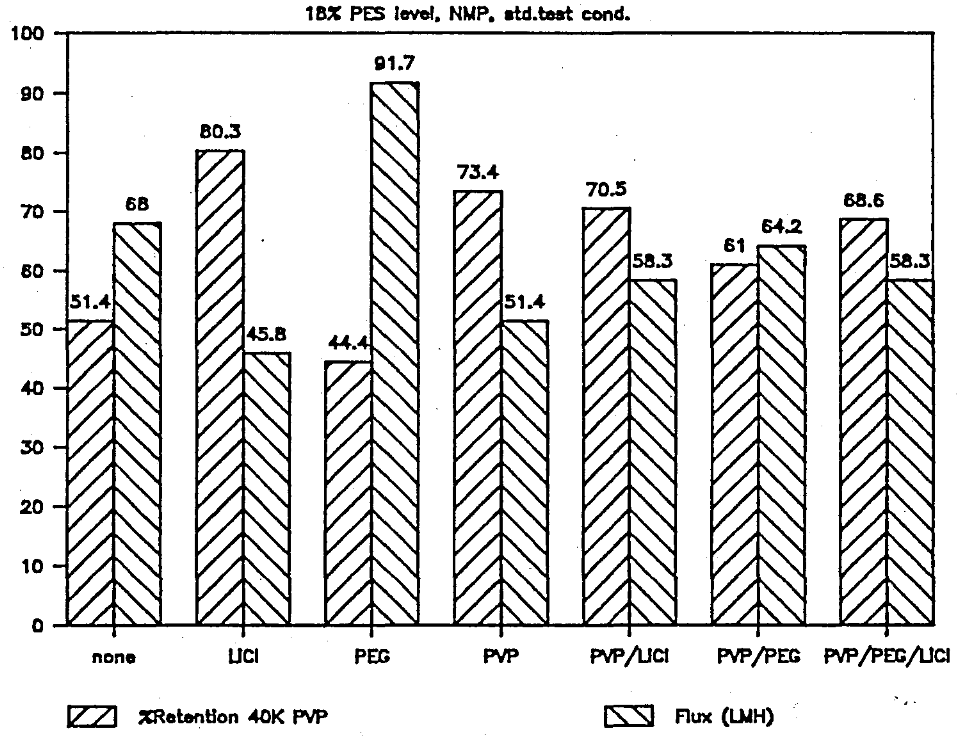
Although a large variety of other substances have been used by other workers for controlling pore size and pore distribution in membranes, it is felt that by the use of the few selected chemicals mentioned above, membrane performance can be adequately adjusted and controlled in a practical manner.

TABLE 5.4 PERFORMANCE OF MEMBRANES PREPARED FROM VARIOUS CASTING SOLUTIONS

(Membranes were made under identical conditions and tested at standard test conditions on PVP of 40 000 MM)

SAMPLE	CASTING SOLUTION COMPOSITION					FLUX	RETENTION
NO.	%PES	%NMP	%PVP	%PEG	%LiCℓ	($\ell m^{-2} h^{-1}$)	(%)
1	14,0	86,0				276,7	17,8
2	18,0	82,0				68,0	51,4
3	14,0	85,8			0,2	58,3	56,2
4	18,0	81,8			0,2	45,8	80,3
5	14,0	81,0	5,0			69,5	43,4
6	18,0	77,0	5,0			51,4	73,4
7	14,0	84,0		2,0		54,2	60,1
8	18,0	80,0		2,0		91,7	44,4
9	14,0	83,8		2,0	0,2	134,6	15,6
10	18,0	79,8		2,0	0,2	67,9	71,2
11	18,0	75,0	5,0	2,0		64,2	61,0
12	18,0	74,8	5,0	2,0	0,2	58,3	68,6
13	18,0	76,8	5,0		0,2	58,3	70,5

FIGURE 5.4
Effect of casting solution composition on membrane performance



5.4 EFFECT OF STORAGE ON MEMBRANE PERFORMANCE

The fact that membrane characteristics changed with time was realised during the very early stages of membrane development, but was never substantiated at the time.

An experiment was conducted in which freshly fabricated membranes were stored under normal conditions. The membranes were characterised in their fresh state and again after 200 days of storage.

5.4.1 METHODS AND MEASUREMENTS

Storage medium: The ultrafiltration membranes were stored in a stainless steel rinse tank which received a continuous supply of RO permeate obtained from Paarl tap water (ROTAP). Typical average values for this type of water are pH 8,5 and a residual chlorine level of not more than 0,5 ppm. Under these conditions the membranes remained essentially slime-free and showed no microbial growth on their surface. Water temperatures varied from 10 to 17 °C.

Membrane characterisation: Membranes were characterised by measuring pure water flux, as well as observed retention and flux in a standard filtration (challenge) test using PVP of 24 000 molecular mass.

Pure water flux measurements: Throughout the experiment, pure water flux was measured on six random samples drawn from the batch of membranes. These samples were tested in individual test cells and an average flux value for the six samples was computed.

5.4.2 RESULTS AND DISCUSSION

Retention: Retention measurements were recorded two days after membrane manufacture (required leach period is 48 hours) and again after 200 days of storage. At standard test conditions, using a test solution of PVP with a molecular mass of 24 000 the following results were obtained for the 713 membrane type:

Storage time (days)	Retention (%)		Flux ($\ell m^{-2}h^{-1}$)	
	average	std. dev.	average	std.dev
2	4,2	0,3	237,5	11,7
200	40,0	6,6	23,8	2,9

Retention had thus increased by a factor of approximately ten while flux had decreased correspondingly.

Pure water flux: Pure water flux values show a very steep decrease during the first 20 days of storage after which they level out to become a constant after roughly 100 days of storage. The difference in flux at day 100 and day 200 is marginal and the membranes can be regarded as stable. The flux decline curve is illustrated in FIGURE 5.5.

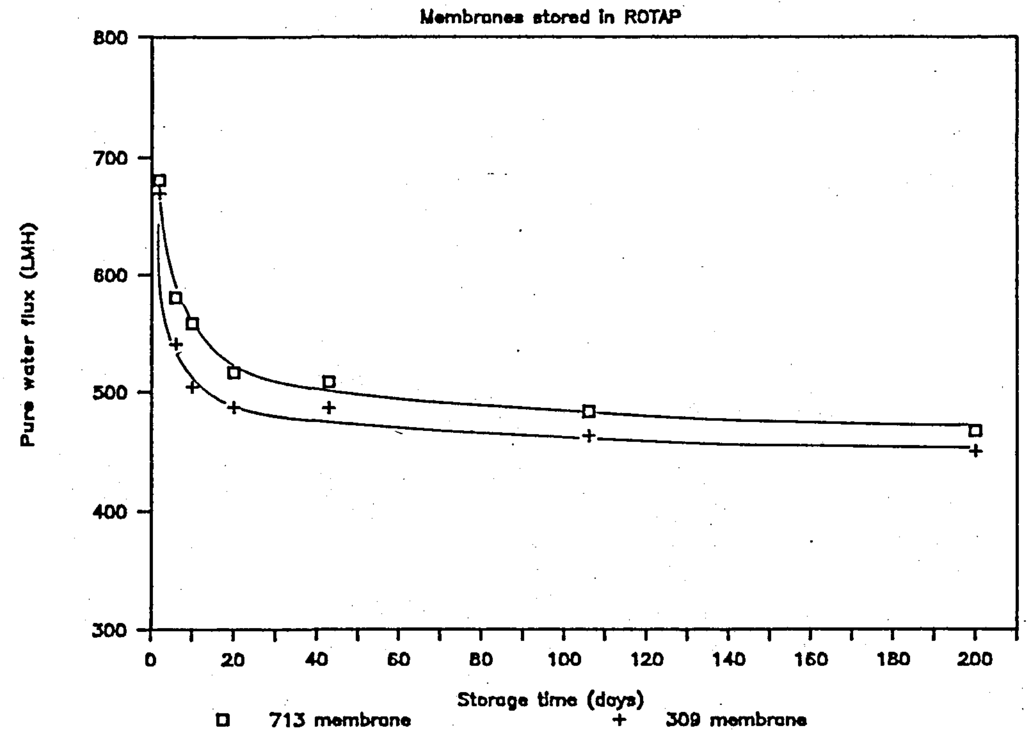
Discussion: The fact that retention increased with a similar factor by which flux decreased would suggest a densification of the entire membrane structure with a resultant uniform reduction of skin pore size. This fact seems to be substantiated by the similar shape of the pure water flux decline curves for the two different membrane types (types 713 and 309). Since dissimilar membranes have different pore size distributions, the densification effect must be uniform in order to give resulting flux decline curves of similar shape.

The steep decline in flux during the first twenty days of storage can be attributed to the leaching of residual solvent trapped in the membrane structure during gelation in the manufacturing process, which results in membrane shrinkage. The slow leaching of the entrapped solvent causes the formation of new polymer-rich and polymer-poor regions with a resultant structural change. After twenty days, practically all solvents and additives were leached from the membrane and the membrane morphology could be regarded as stable.

Initial characterisation measurements therefore do not give an indication of true future membrane performance and should ideally be done only after freshly manufactured membranes have been allowed to leach for a minimum of twenty days. It should be possible, however, to increase the rate of the process by raising the temperature of leaching (storage) medium.

FIGURE 5.5

Pure water flux *vs.* storage time for ultrafiltration membranes



5.5 HYDROLYTIC STABILITY OF UF MEMBRANES

5.5.1 INTRODUCTION

In order to determine the chemical stability of UF membranes with regard to pH variations, stability experiments were conducted. Tube stabilities in solutions of high and low pH were determined and the effect thereof on the polyester support fabric was investigated.

Although the excellent resistance of polysulfone to chemical degradation is well known, it was felt that the membrane tube as a whole should be investigated under static as well as actual dynamic operating conditions. Almost all stability tests described in the literature are concerned with static test methods that provide no information on membrane stability in service.

Generally, membrane samples were subjected to various aqueous solutions at elevated temperatures to simulate accelerated degradation. Using the commonly accepted rule that chemical reaction rates double for every 10 °C temperature increase, an equivalent life expectancy is obtained for less severe operating conditions *(Spatz and Friedlander, 1978)*.

Nevertheless, although the procedure is tedious, the best stability data are obtained from long term dynamic operation of the membrane on the test solution.

5.5.2 PROCEDURE

The object of this experiment was to determine the stability of membrane tubes when in contact with feed solutions of high and low pH . Since caustic solutions are frequently used as a cleaning medium to restore flux values in fouled UF membranes, information on the stability of membranes with regard to pH variations had to be obtained.

One of the main difficulties associated with stability tests is obtaining meaningful "before" and "after" test data. Use of the same piece of membrane for the baseline performance data, the trial conditions, and the post-trial performance data, incurs the risk of physically damaging the sample due to excessive handling.

This problem could be solved by using one sample of the membrane for the original test data and another for the stability trial and post-testing. However, there are sometimes variations between neighbouring areas of the same sample of membrane and these could be large enough to mask any change due to the trial environment. A better approach is to keep the sample in one test cell for the entire test. This requires extra expense and time since only one solution can be tested at a time, but the quality of the data collected could be improved substantially.

Membranes were tested in perforated stainless steel tubes to facilitate easy removal and inspection after the completion of the experiment. Baseline performance data were obtained from fresh membrane samples before they were subjected to the feed solution. Flux values were determined to observe tube deterioration with time. After completion of the test, intact remaining tubes were characterised once more in order to determine whether there had been membrane degradation. Six tubes were tested at a time and kept in the same cells throughout the test.

SEM micrographs of "before" and "after" membrane samples were taken to determine structural changes in the membrane.

5.5.3 DYNAMIC TESTS

Dynamic pH stability tests were carried out at values of pH 1, pH 10 and pH 12. The solutions used to determine the resistance of the tubes to hydrolysis were prepared by addition of either sulphuric acid or sodium hydroxide to ROTAP until the desired pH was obtained. The pH of the solutions was checked daily and adjusted if required.

Average operating conditions were:

Feed pressure	500	kPa
Feed temperature	30	°C
Linear velocity	0,5	$m\ s^{-1}$

5.5.3.1 *Membrane performance*

For all membranes the retention increased and the flux value decreased when tests were done on 40 000 MM PVP in a standard challenge test. Relevant results are shown in TABLE 5.5. It is thought that this was not due to the effect of NaOH or sulphuric acid on the membrane, but rather the result of the densification due to time and pressure effects (refer to densification experiments described in section 5.4).

SEM investigation of membrane samples indicated that the PES membrane substructure was unaffected by pH conditions (*i.e.* hydrolysis) and that tube failure could be attributed to hydrolysis of the polyester fabric.

TABLE 5.5 MEMBRANE PERFORMANCE DATA BEFORE AND AFTER DYNAMIC pH TESTS : STANDARD TEST RESULTS (40 000 MM PVP)

pH	Retention (%)		Flux ($\ell m^{-2}h^{-1}$)	
	before	after	before	after
12,0	51,0	73,6	58,3	41,3
10,0	46,0	70,0	75,4	67,5
1,0	45,1	69,0	70,8	53,3

5.5.3.2 *Tube performance*

Support tube integrity was unaffected at lower pH values. After 520 hours of operation at pH 1 and pH 10 the polyester support tubes showed no deterioration. At pH 12 however, the first tube failure occurred after 102 hours of operation with subsequent failures after 125 hours. In all cases the failure could be attributed to weld-seam failure which in turn caused despiralling of the polyester support tube. Since the weld-seam is a highly stressed part of the tube and polyester itself (being an ester) is known to hydrolyse at high pH conditions, the subsequent weld-seam failures were to be expected.

To confirm that the failures were due to hydrolysis and not poor weld-seam quality, fresh tube samples from the same batch were subjected to tensile stress tests. The strengh of the weld-seam on these tubes fell within normal limits.

The failure could therefore be attributed with relative confidence to hydrolysis of the polyester support, in particular weld-seam failure, due to hydrolysis at high pH.

Flux *vs*. time curves for the different pH solutions are shown in FIGURES 3.4 to 3.6.

FIGURE 5.6
Flux *vs*. time for pH 1

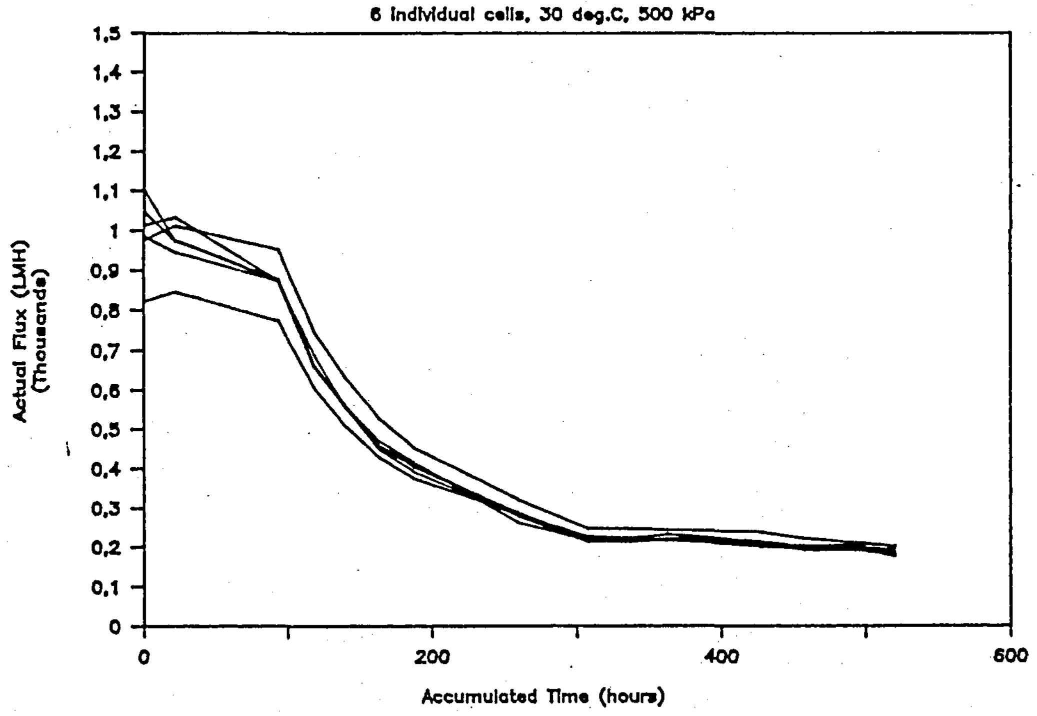

6 individual cells, 30 deg.C, 500 kPa

FIGURE 5.7
Flux *vs*. time for pH 10

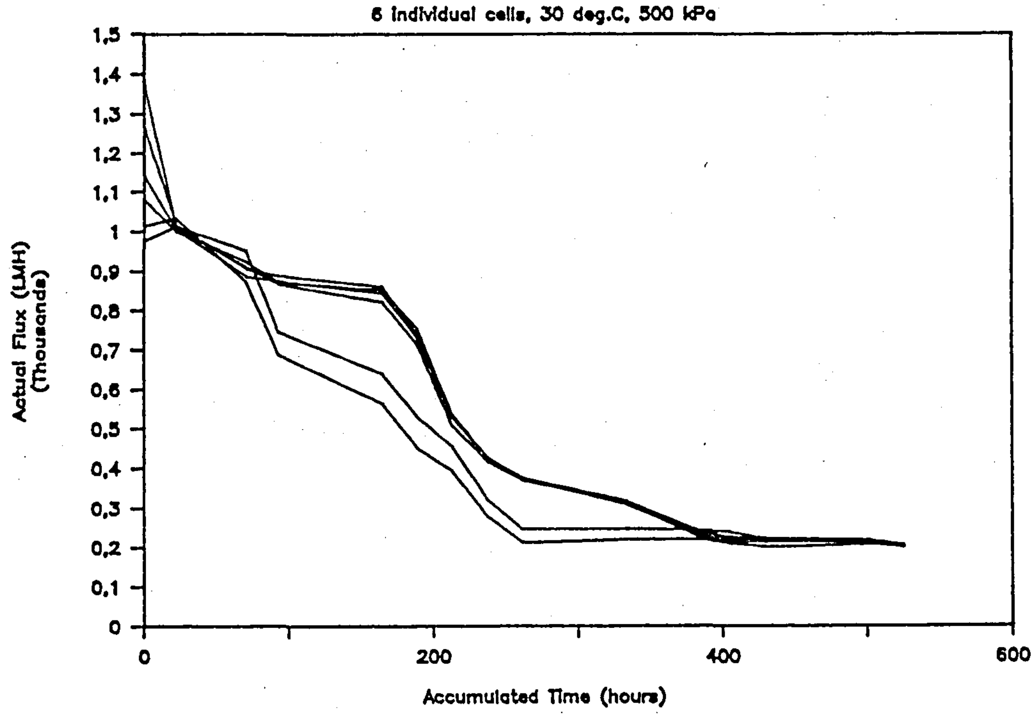
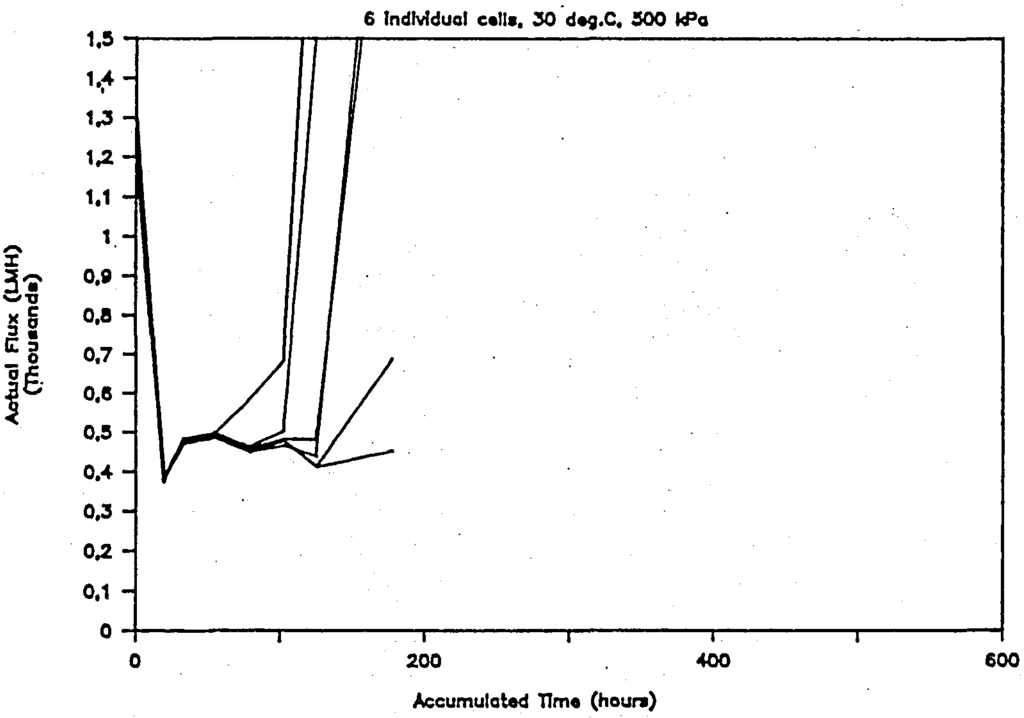

6 individual cells, 30 deg.C, 500 kPa

FIGURE 5.8

Flux *vs*. time for pH 12



5.5.4 STATIC TESTS

After the dynamic tests had provided first-order information with regard to pH limitations, it became necessary to study the effect of pH on membrane performance in more detail and to obtain information with regard to membrane stability during long-term exposure.

From the results of the dynamic tests the safe pH operating range was taken as 1 to 11. Therefore, membrane samples were encapsulated in containers with different buffer solutions and placed in a waterbath at 60 °C for 50 days. According to *Spatz and Friedlander (1978)* this should give an expected equivalent exposure of 16 to 20 months at 25 °C.

The experiment also enabled comparisons to be made of experimental membranes and commercially available UF membranes with regard to performance and stability. The obvious choice fell on Patterson Candy International (PCI) because these membranes have similar physical dimensions, and also because of their highly acclaimed standard of quality. In particular the PCI BX3 UF membrane was selected since these membranes are made of similar material (polysulfone), and were reported to have similar retention and operating characteristics.

Experimental and PCI BX3 membranes were subjected to identical conditions during the experiment and characterisation procedure. Membrane performance data obtained, using the standard test method, before and after the static pH experiment, are shown in TABLE 5.6.

Both retention and flux values for the PCI membranes had deteriorated after exposure to the various pH solutions. At pH 5 however, both retention and flux showed a slight increase. For the experimental membranes, both retention and flux showed an increase, except at pH 7 at which both retention and flux showed a slight decrease.

Retention values for both PCI and experimental membranes are illustrated in FIGURE 5.9 as the ratio between "after" and "before" values in the pH 1 to 11 range, while flux ratios are shown in FIGURE 5.10. A value above 1 therefore indicates an increase in retention and *vice versa*. The obvious discrepancy at pH 7 for both PCI and experimental membranes could possibly be attributed to chemicals present in the buffer solution which might have had an adverse effect on the membranes.

In general, it follows that the experimental membranes were not adversely affected by hydrolysis in the pH 1 to 11 range and should have an expected economical life of two to three years in this pH range under normal operating conditions.

With regard to stability in comparison with that of PCI BX3 membranes, the experimental membranes can be regarded as being on a par with one of the best commercially availble UF membranes.

TABLE 5.6 MEMBRANE PERFORMANCE DATA BEFORE AND AFTER STATIC pH TESTS : STANDARD TEST RESULTS (40 000 MM PVP)

		PCI BX3			TYPE 713		
pH		BEFORE	AFTER	A/B	BEFORE	AFTER	A/B
1	retention	62,3	50,0	0,8026	27,9	35,6	1,2760
	flux	22,3	19,8	0,8879	10,2	20,0	1,9592
3	retention	73,6	56,4	0,7663	31,9	48,6	1,5235
	flux	21,3	16,3	0,7647	10,4	26,3	2,5200
5	retention	57,8	65,9	1,1401	27,8	46,2	1,6619
	flux	17,9	25,0	1,3953	9,2	19,8	2,1591
7	retention	68,9	45,4	0,6589	4,5	38,5	0,9277
	flux	17,9	19,8	1,1047	29,8	21,7	0,7273
9	retention	63,6	53,2	0,8365	35,9	43,6	1,2145
	flux	12,9	18,3	1,4194	35,0	41,3	1,1786
11	retention	71,0	52,8	0,7437	18,8	40,4	2,1489
	flux	22,7	24,6	1,0826	16,5	27,7	1,6800

A/B = ratio between after and before retention/flux values

Retention values are given in % and flux values in $\ell m^{-2}h^{-1}$

FIGURE 5.9
Retention ratio comparison at various pH values

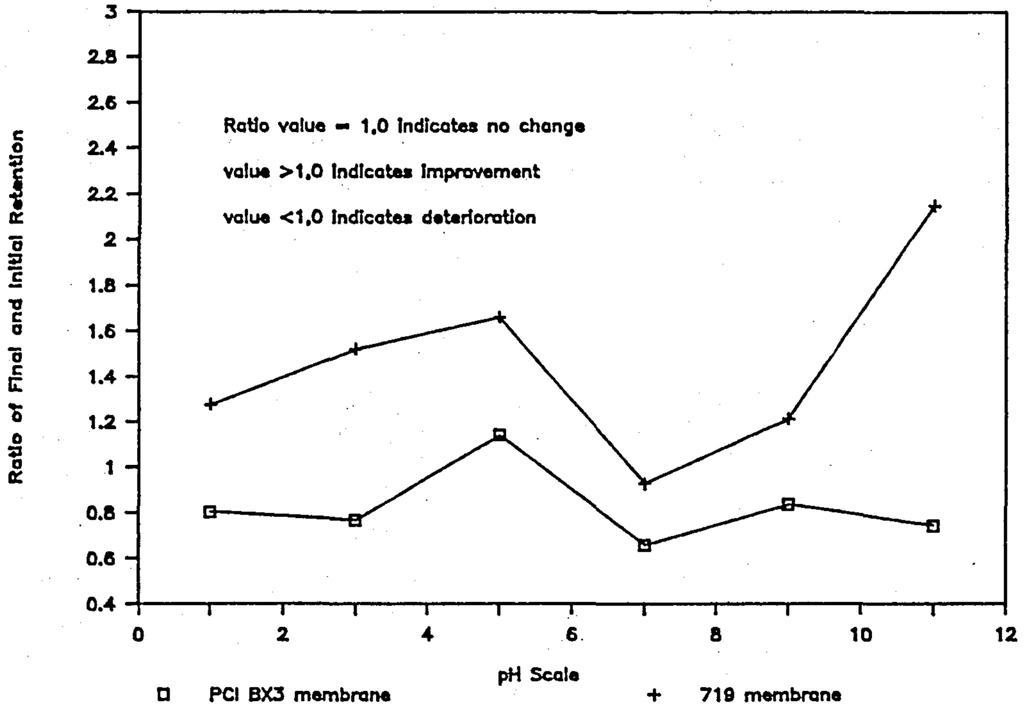
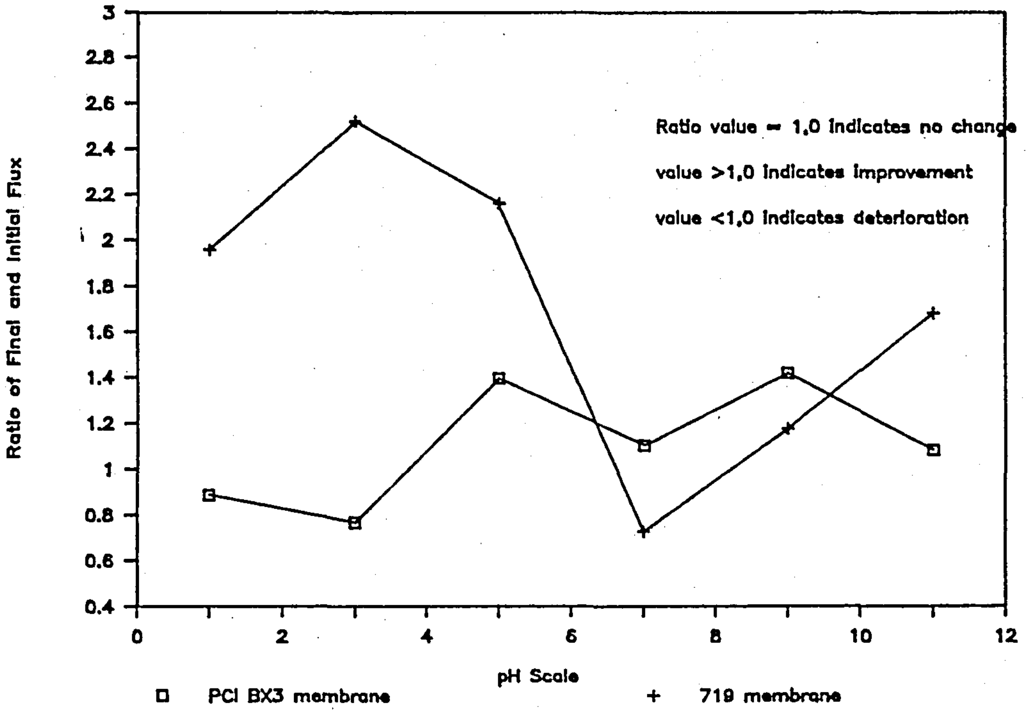


FIGURE 5.10
Flux ratio comparison at various pH values



5.6 EFFECT OF SOLUTE CONCENTRATION IN COAGULATION TANK ON MEMBRANE PERFORMANCE

The addition of solvent to the coagulation tank resulted in membranes with increased flux and decreased retention (refer to section 4.2.2) At levels above 50% solvent content in the coagulation bath, flux values were found to increase dramatically with a corresponding decrease in rejection (TABLE 5.7). With increasing solvent concentration in the coagulation bath, the membrane structure changed gradually from asymmetric to symmetric. This approach could possibly be used to fabricate polyethersulphone UF membranes which can be stored in a dry state as outlined in the literature *(Wafilin, 1983)*.

TABLE 5.7 EFFECT OF SOLVENT CONCENTRATION IN COAGULATION TANK ON MEMBRANE PERFORMANCE : STANDARD TEST RESULTS (40 000 MM PVP)

NMP concentration (%)	Retention (%)	Flux ($\ell m^{-2}h^{-1}$)
0	85	47,5
30	66	50,4
50	17	84,6
70	0	214,6

Membranes prepared from a casting solution containing 18% PES by mass in NMP.

5.7 PERFORMANCE UNDER PROCESS CONDITIONS

As mentioned previously, observed rententivity data cannot be used directly to select and predict membrane characteristics and performance on complex feed streams. Membrane performance and selectivity is strongly dependent on the nature of the feed stream and its composition, and on the operating conditions, membrane material and configuration.

Initial characterisation data (alternatively data obtained by quality control methods) can be used only to distinguish between membrane types produced in-house and to select the best possible candidate membrane for a certain application. The applicability of the selected membrane will then have to be tested under actual process conditions. In some cases it might even be necessary to tailor the most suitable available membrane to the particular application. Results obtained with experimental membranes on real process streams are reported in CHAPTER SEVEN.

CHAPTER SIX

MODULE DESIGN AND EVALUATION

6.1 INTRODUCTION

In order to be of practical use, the tubular UF membranes have to be supported mechanically in an adequately designed housing for the following reasons:

- i) the membranes must be contained in a pressure vessel of some kind to prevent expansion and rupture of the tubes when subjected to operating pressures;
- ii) the membranes must be protected from mechanical damage from the outside by physical means during handling and installation;
- iii) the membranes must be contained in a vessel of some kind which will prevent drying of the membranes, which would cause a loss of permeability;
- iv) permeate from individual tubes must be collected and in certain cases be prevented from contamination by foreign matter.

It follows that the tubular membrane assembly must serve two functions, *i.e.* as a membrane support device and as a permeate collection vessel. In addition provision must be made for interconnection of the membrane assembly (module) to an identical device and for internal manifolding of the individual membranes within the module for proper flow configuration.

When a module is referred to, the membrane tube assembly fitted with membrane tubes, is implied. As such, a module is a self-contained unit, and can be viewed as a building block for the construction of a filtration system. Design and construction of a module are discussed in more detail in the next paragraph.

6.2 MODULE CONSTRUCTION

The assembly of tubular membrane filter modules can be cumbersome and expensive, as regards tube support structure and interconnecting/sealing of the ends of the membrane tubes. Many commercial manufacturers of membrane systems use perforated stainless steel or porous glass fibre tubes to provide external pressure support for the tubular membrane. When the cost of such stainless steel or glass fibre tubes is combined with the cost of the traditional machined heads, providing the connecting manifolding for the individual membrane tubes, this practice is rather costly.

For the presence of the study, two types of modules can be distinguished, *i.e.* modules for food treatment and modules for effluent/water treatment. The basic design of the different modules is identical, the difference being the manner in which the ends of the membrane tubes are sealed, anchored and connected.

Polymeric discs, which may be made of punched-out or injection-moulded engineering plastics, are arranged in a side-by-side pattern inside the tubular housing (FIGURE 6.1). The type of engineering plastic depends on the intended application for the module. The discs have holes in them of similar diameter as that of the membrane tubes, and are in alignment to define elongated passages. The membrane tubes are inserted into these passages. Each disc has nineteen (19) of these holes, *i.e.* each module therefore contains nineteen membrane tubes, each with a diameter of 12,7 mm. Adjacent to the last disc on either side, is a sealing disc. The ends of the membrane tubes pass through the sealing discs and protrude for a short distance *(Bakke, 1980)*. A collection of these stacked discs with membrane tubes inserted into the aligned holes, is placed inside a tubular housing which serves as a pressure- and permeate-collection vessel.

The ends of the membrane tubes are interconnected by means of U-shaped interconnection bends. These bends fit into the ends of the tubes and are arranged in such a way as to create one continuous passage (FIGURE 6.2). This arrangement is referred to as a series connection of membrane tubes. For parallel connected membrane tubes, a conical reducing cap is placed over the tube ends to act as a manifold (FIGURE 6.3). When the discs have been assembled and provided with membrane tubes and U-bend connectors, or alternatively, reducing cones, they are inserted into a tubular housing.

For treatment of effluents and other non-sanitary liquids, the tubular housing is provided with an internal recess at both ends of the housing. The recess, which may be a spiral groove, provides anchoring for the resin casting in which the U-bend connectors (alternatively, conical reducers) and parts of the membrane tubes are embedded (FIGURE 6.4).

For treatment of food, this procedure for end-cap sealing was modified since the tubular housing material was costly as it had to be of a quality to comply with food industry specifications. The problem with the system for effluent application was that, for preparing the assembly for reuse (membrane replacement), the epoxy castings had to be machined out of the tubular housing. At times the grooved section of the tubular housing was damaged during this machining step, rendering the housing useless. Another problem was that the thickness of the wall of the tubular housing had to be adquate to allow for the cutting of the grooves, which contributed to high material cost.

These problems were overcome by employing a floating head similar to the concept used in heat exchanger design *(Kern, 1950)*. Two removable bushes were located at each end of the tubular housing (usually stainless steel). One side of each bush fitted onto one of the two end-discs of the membrane tube assembly. Resin was cast into each bush (alternatively, reducing cone) to embed the U-bend connectors and parts of the membrane tubes which projected beyond the end disc. The bushes (alternatively, reducing cones) were locked removably in the tubular housing by means of a circlip and annular groove in the housing. A further groove in each of the tubular bushes (alternatively, reducing cones) accepted an O-ring which acted as seal between the permeate collected inside the tubular housing and the environment (FIGURES 6.2 and 6.3). The tubular housing further provided a draining tube for the removal of permeate from the annulus between the polymeric disc assembly and the tubular housing.

The liquid to be filtered is supplied from one end of the module into one membrane tube, or by way of a manifold into a number of membrane tubes, and passes along the tubes to be filtered through the UF membrane and support tubes. The filtered liquid is then withdrawn from the annulus between the polymeric discs and the housing. The liquid which remains inside the tubes (concentrate) passes through a discharge outlet at the other end of the module.

FIGURE 6.1
Illustration of support disc

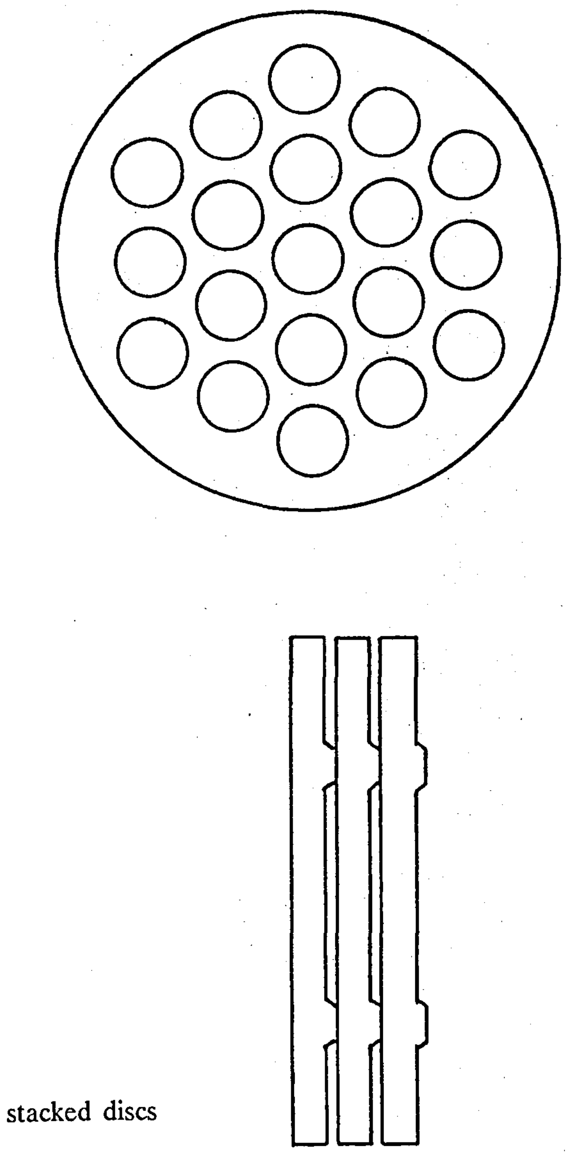


FIGURE 6.2
Food application module : series tube connection

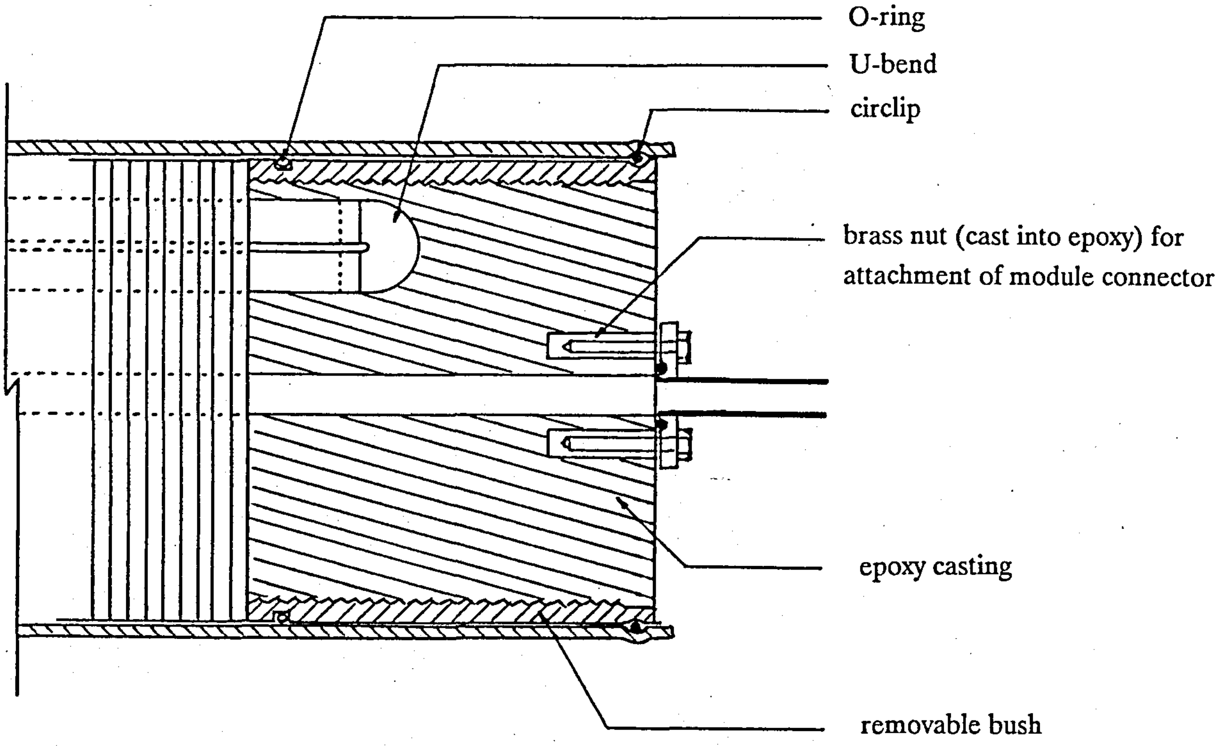


FIGURE 6.3
Food application module : parallel tube connection

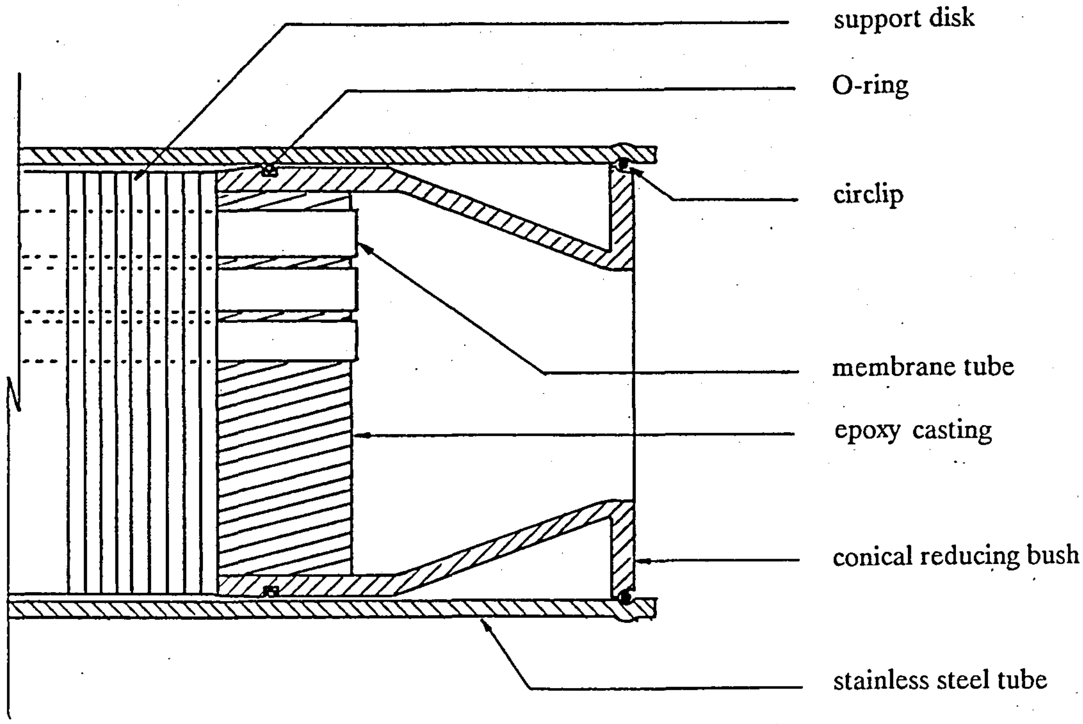
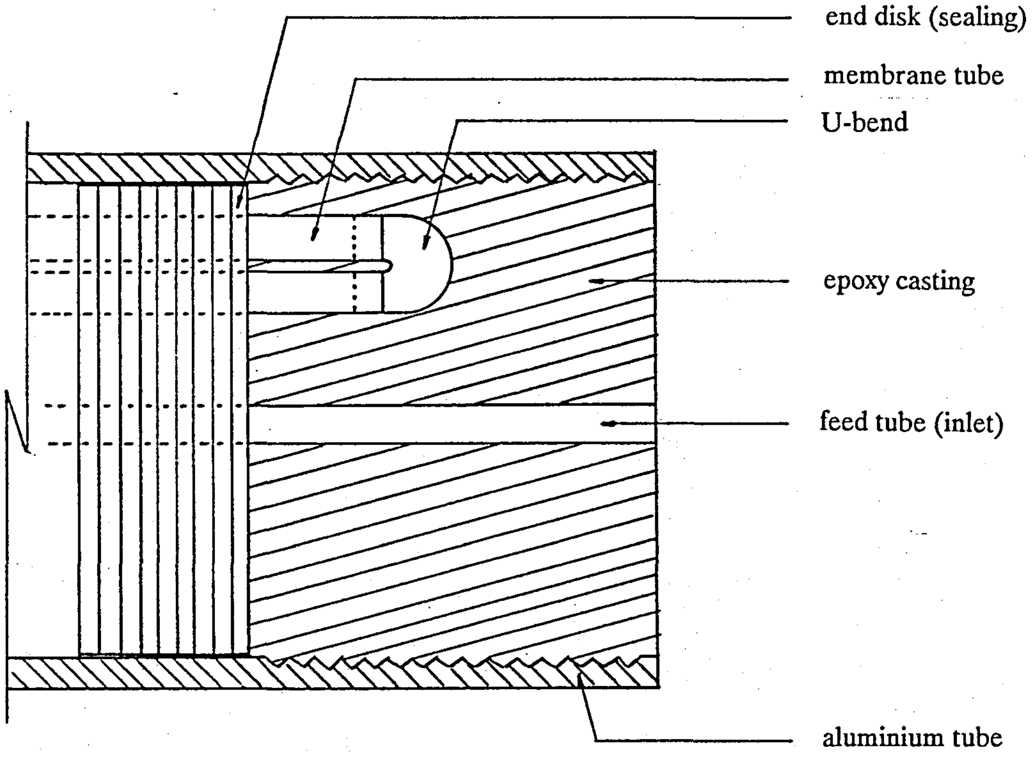


FIGURE 6.4
Water/effluent application module : series tube connection



6.3 MATERIALS OF CONSTRUCTION

Construction materials to be used in the manufacture of modules must meet two main requirements.

First, and most important, the materials used must be compatible with the feed solution of the intended application. This implies resistance against corrosion and against deterioration of mechanical strength (fatigue, stress cracking *etc.*) during prolonged use. Not only should these materials be compatible with the feed solution, but also with the proposed cleaning solutions.

Second, the materials must not affect product (either permeate or concentrate) quality, particularly in food processing.

6.3.1 FOOD APPLICATIONS

When foodstuffs are processed for human consumption, the process equipment and its components usually have to comply with standards laid down by health laws to ensure proper product quality.

Since the use of processing equipment manufactured from stainless steel has become the norm in the food industry, it was decided to employ stainless steel for the tubular housing in modules for food treatment. This serves several purposes, the most important being to create the client's confidence in the technology, as well as satisfying the asthetic and durability aspects.

Personal experience has shown that the client usually has some scepticism towards membrane technology, because of his ignorance of the process, so that the use of engineering plastics in visually apparent module components is observed with doubt. The use of a familiar and tried material such as stainless steel aids in gaining the client's confidence towards the technology. The tubular housing, bushes and module connection bends are thus manufactured from stainless steel, usually grade 304 or grade 316 for special applications. Polycarbonate was chosen from engineering plastics such as ABS, polypropylene and NORYL™ (polyphenylene oxide) as a construction material for the polymeric discs used in the membrane tube assembly because of its food grade properties, physical and injection-moulding characteristics as well as resistance to chemical attack by various cleaning solutions. An epoxy resin with food grade properties is used for the end castings.

6.3.2 WATER APPLICATIONS

The use of specialised food-grade module construction materials in the treatment of water and effluent is not justified by the value of the end-product (either permeate or concentrate) produced by such modules. Since the clarified water or effluent has little or no added value, module components for such applications should be as cheap as possible without any sacrifice of durability or engineering requirements. Since the liquid product from such modules is not usually intended for human consumption, module components need not be manufactured from materials that comply with food-grade specifications.

Greater emphasis was therefore placed on the durability and cost effectiveness of the module assembly. Asthetic appeal, although secondary, was nevertheless also considered to be important since the use of membrane technology is generally viewed as a so-called "high tech" filtration application.

Marine-grade aluminium tubes are used for the tubular module housing due to their resistance to corrosion (durability), ease of machining and relatively low cost. Anodising or epoxy coating of the tubes results in further protection against corrosion as well as in improving appearance.

For ultra-low budget applications, the use of PVC pipes for tubular housings may be considered, due to the substantially lower cost of this material compared with that of aluminium.

Polymeric discs used for the membrane tube assembly are injection-moulded from either ABS (acrylonitrile/butadiene/styrene co-polymer), NORYL™ (polyphenylene oxide) or polypropylene, depending on the requirements of the particular application.

6.4 EVALUATION OF MODULES

After assembly of module components and the required curing period for the epoxy end-castings, each module must be subjected to a quality-assurance test prior to leaving the factory.

During this test, the modules are inspected for visual defects and appearance, as well as for mechanical and membrane integrity. Quality control serves two major purposes, first, to reduce the amount of reject modules produced and, second, to ensure that a sound end product leaves the factory. Cutting down on the amount of rejects produced serves to improve the yields of membrane raw materials used, *i.e.* production cost. In ensuring that a sound product leaves the floor, the customer is protected against subsequent loss, and unnecessary scrapping of defect modules by the manufacturer is prevented.

6.4.1 MECHANICAL TEST

Since the newly manufactured ultrafiltration modules are destined for use by the customer, routine quality assurance tests must be non-destructive. Nevertheless, the test must be stringent enough to eliminate modules that are below specification.

The test for mechanical integrity comprises two distinct, simple tests which are designed to show major production errors immediately.

To check the flow pattern of a series-connected module, a spongeball is inserted at one end of the module, and the module is then flushed with water from that particular end of the module. If all the turn caps (U-bends) have been placed correctly, all the tubes in the module will form a single elongated passage, resulting in ejection of the sponge ball at the other end of the module.

The flow passages of parallel modules are inspected visually since all tubes are parallel with one another, defining a once-through passage.

The integrity of other module components as a functional unit is checked with a high-pressure test. Since the operating pressure is usually limited to a maximum of 600 kPa (due to pump considerations, since the cost of most pump types increases by a factor of about two above 600 kPa and flux rates usually do not show a substantial increase at pressures above this figure), the high pressure test is performed at 800 kPa. Since test pressures at values above 1 000 kPa can result in unwanted, excessive compaction of the ultrafiltration membrane the intermediate value of 800 kPa was selected for hydraulic testing of modules.

6.4.2 INTEGRITY TEST

Since random membrane samples are characterised in terms of retention and flux with the aid of PVP solutions, modules are not subjected to this test due to its tediousness.

Instead, modules are subjected to an integrity test by use of a solution of ROTAP and Congo Red dye, as a test similar to that used for individual membranes. Although Congo Red dye has a molecular mass of only 696 g mol^{-1}, the dye is retained completely by the membranes. This fact is contradictive to the fact that UF membranes do not retain low-molecular mass substances and can possibly be explained by taking charge effects into account. Charge effects could result in the conglomeration of individual dye molecules to such an extent that these conglomerates are too large to pass the membrane. Whatever the case might be, fact is that the dye is retained by the membrane. Therefore the slightest passage of dye immediately indicates a retention defect in the module.

CHAPTER SEVEN

BENCH/PILOT STUDIES

7.1 INTRODUCTION

The goal of the research and development work discussed in the previous chapters of this thesis, was to evaluate the technology in an industrial environment. This was achieved by subjecting the membranes to various feed solutions during bench and pilot plant studies in the laboratory as well as in the field. Bearing in mind the traditional application fields for UF, outlined in CHAPTER TWO section 2.5, three major application divisions were realised, namely, water filtration, food and effluent treatment.

In water treatment, UF is used to clarify and filter raw water to be used (i) in the manufacture of a product, or (ii) for the reclamation of process water. Typical examples for the first case are clarification of river or dam water to be used for cooling purposes or filtration of tap water to be used for product preparation in the beverage and canning industry. Polishing of boiler feed water or steam condensate for reuse, are examples of the second case.

Studies concerned with food applications were limited to clarification and protein stabilisation of fruit juices, dairy applications and concentration of egg products.

Other studies involved the purification of various effluents from several industries.

The main objectives during a bench study or extended field trials were:

i) qualitative determination of product quality;
ii) determination of flux values;
iii) determination of pressure, temperature, recovery effects on flux values;
iv) optimisation of operating parameters;
v) determination of membrane cleaning regimes;
vi) determination of operating cost, if possible.

Product quality

The first step in determining whether the UF process was applicable was to obtain UF permeate and/or concentrate and to evaluate their quality for comparison with the required standard.

Flux values

The next step was to determine flux values at fixed operating conditions.

Pressure, temperature and recovery

The effects of operating variables on flux were usually interdependent and had to be investigated individually. This was done by varying one operating parameter at a time while keeping all others constant, if possible. The effect of each individual variable was then correlated against flux.

Optimisation of operating parameters

Once the correlations between individual operating parameters and flux had been determined and described in mathematical terms, operating conditions could be optimised to provide maximum, economical flux values.

Cleaning regime

A cleaning technique to restore flux values after fouling of the membranes, was usually determined by trial and error due to the diversity of foulants and degrees of fouling encountered in practice.

Operating cost

Only once the operating conditions had been determined and a sucessful cleaning regime had been established could a first-order operating cost be determined.

7.2 WATER APPLICATIONS

The fact that UF can successfully provide ultra-clean water for process use is widely accepted in the electronics industry *(Kaszyski, 1980)*. The greatest drawback associated with UF technology in the past, however, has been the high capital cost of such a system. General feed-back obtained from the industry indicated that unless the UF permeate was used directly for the manufacture of a high value product, which dictated the need for a quality of water such as produced by ultrafiltration, the process could not be considered economically viable.

Nevertheless it was the opinion of the author that if a UF system could be manufactured at low cost, direct competition against microfiltration, activated carbon adsorption and ion exchange, with regard to capital and operating costs, should be possible. The advantages of UF would be lower operating cost and virtually no maintenance except for membrane replacement.

The development of such a system and subsequent water purification trials are discussed below.

7.2.1 PURIFICATION OF TAP WATER BY ULTRAFILTRATION

The use of ultrafiltration to purify domestic water supplies aroused interest due to a problem experienced by a manufacturer during the production of polystyrene.

The medium for the polymerisation reaction in the manufacture of polystyrene from styrene monomer, is water. In order to obtain a high quality polymer product, the water used in the reactor has to be of good quality, especially with regard to organic loading. The traditional water purification process used involved sand filtration, followed by activated carbon adsorption, with ion exchange as the final step.

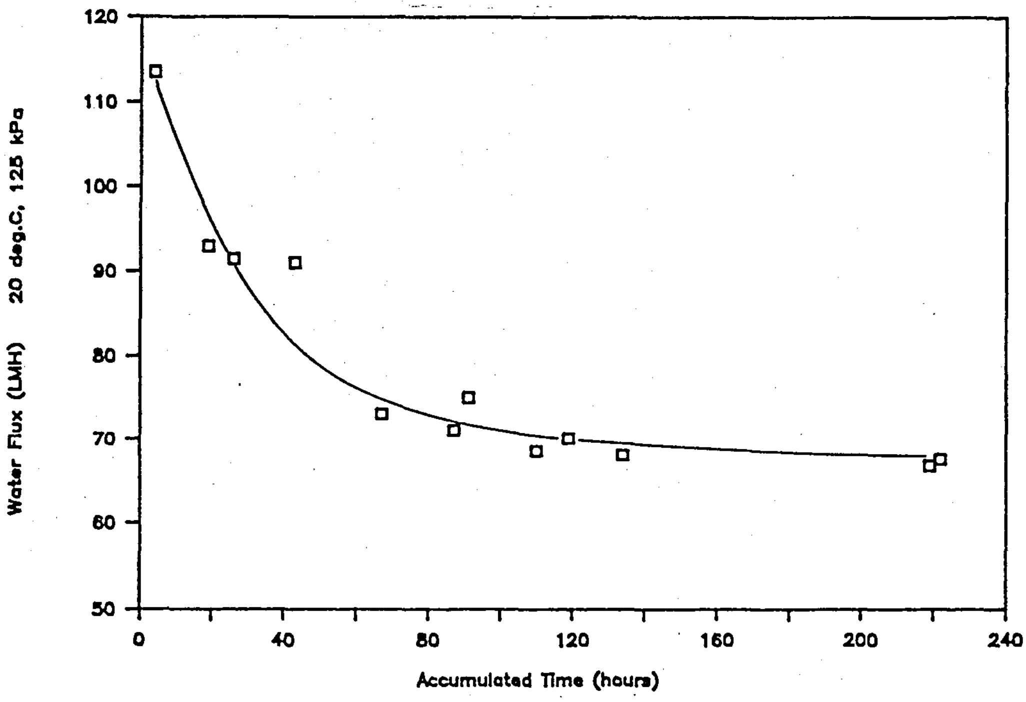
With this purification scheme seasonal fluctuations in polystyrene quality were experienced which were directly attributed to high organic loads in the domestic water supply during rainy periods. During the study, the sand and carbon filter stages were replaced with an ultrafiltration plant containing 10 modules (total membrane area of 20 m^2) connected in such a way to form a single series train. Operating conditions were the following:

feed pressure	200 kPa
feed temperature	ambient
linear flow velocity	2 $m\ s^{-1}$

During the test duration of 220 hours the plant supplied an average of 1,5 m^3h^{-1} of permeate on a continuous basis (refer FIGURE 7.1). This permeate was used during the manufacture of several 6 ton polystyrene batches of excellent quality. The demand for stabilising agent tricalciumphosphate (TCP) was greatly reduced.

A pilot batch of polystyrene using only UF permeate without ion exchange was subsequently produced. Again the quality of the polymer end-product was excellent, TCP consumption was reduced and a narrower polymer bead-size distribution was obtained.

FIGURE 7.1
Flux decline with time on Paarl tap water at polystyrene plant



7.2.1.1 *Ultrafiltration system*

The investigations in the previous paragraph showed the ability of the UF membrane to produce water of good organic quality. The flux decline curve (FIGURE 7.1) was logarithmic and levelled out at approximately 65 $\ell m^{-2}h^{-1}$ at the average operating conditions of 150 kPa and 20 °C.

This indicated that a system of this type could be operated in such a way as to utilise the feed pressure of the water mains.

A subsequent study on Paarl tap water was performed using a three-module cascade system coupled directly to the water mains. The system is illustrated in FIGURE 7.2. It was felt that if long-term flux stability at values of 65 $\ell m^{-2}h^{-1}$, or higher, could be maintained, the resultant system, incorporating low cost modules, could compete favourably with other techniques such as carbon filtration and ion exchange in terms of capital and operating cost. Preferably the system was to operate automatically and with a minimum of maintenance.

A three-module cascade system was operated on a continuous basis to determine the following:

i) flux decline with time
ii) cleaning procedures
iii) automation of operation
iv) economical operating parameters
v) system cost
vi) permeate quality

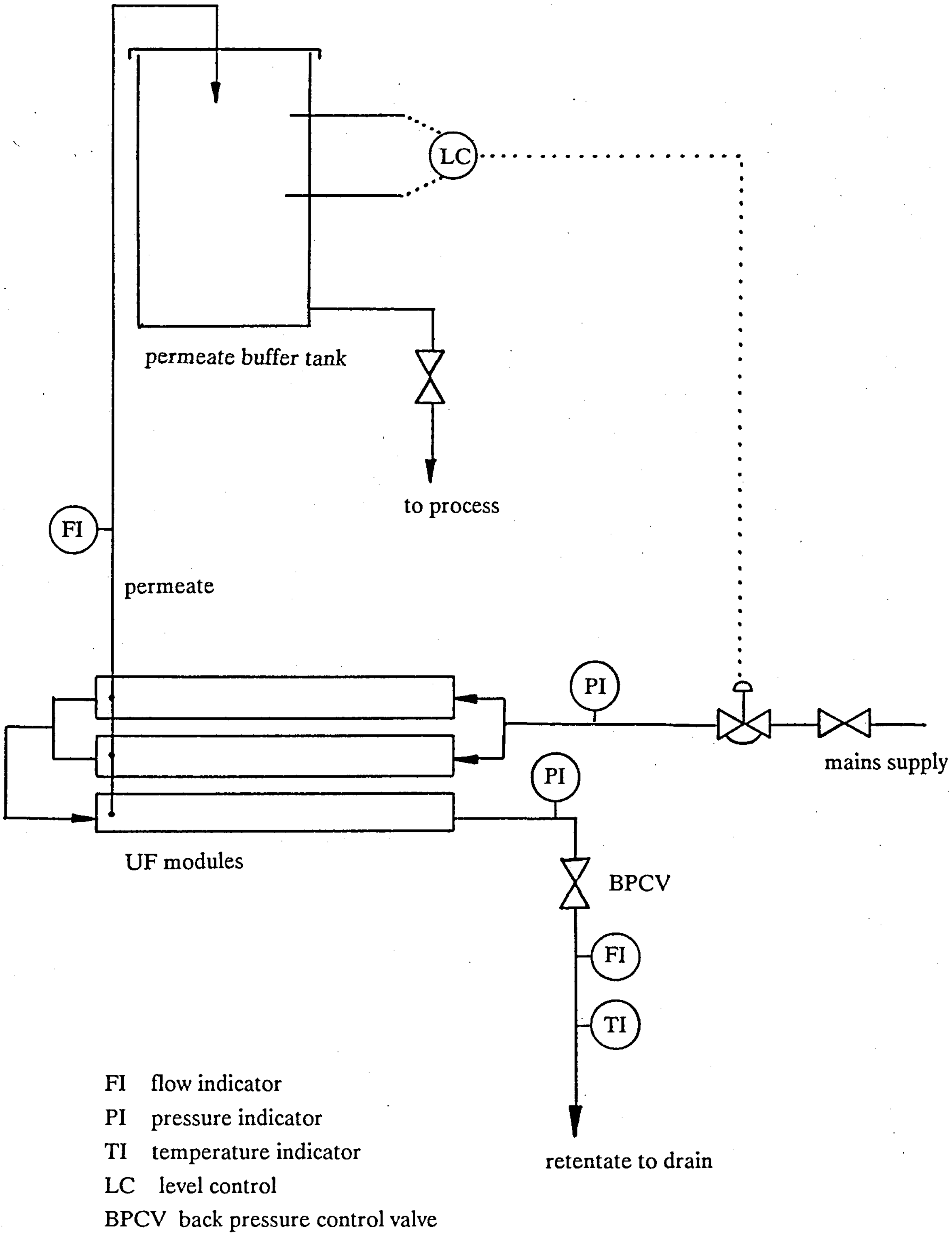
7.2.1.2 *Flux decline for cascade system*

The flux decline rate was reasonably pronounced and from calculations performed on the flux data, which is presented in FIGURE 7.3, was found to be in the region of 5 to 11 $\ell m^{-2}h^{-1}$ per day. The system was operated to achieve constant flux (by increasing the feed pressure) and at a linear flow velocity of 0,5 m s^{-1}. Consequently the trans-membrane pressure difference increased as fouling progressed. The flux values illustrated in FIGURE 7.3 are all corrected to a feed pressure of 100 kPa and a feed temperature of 20 °C.

7.2.1.3 *Cleaning procedures*

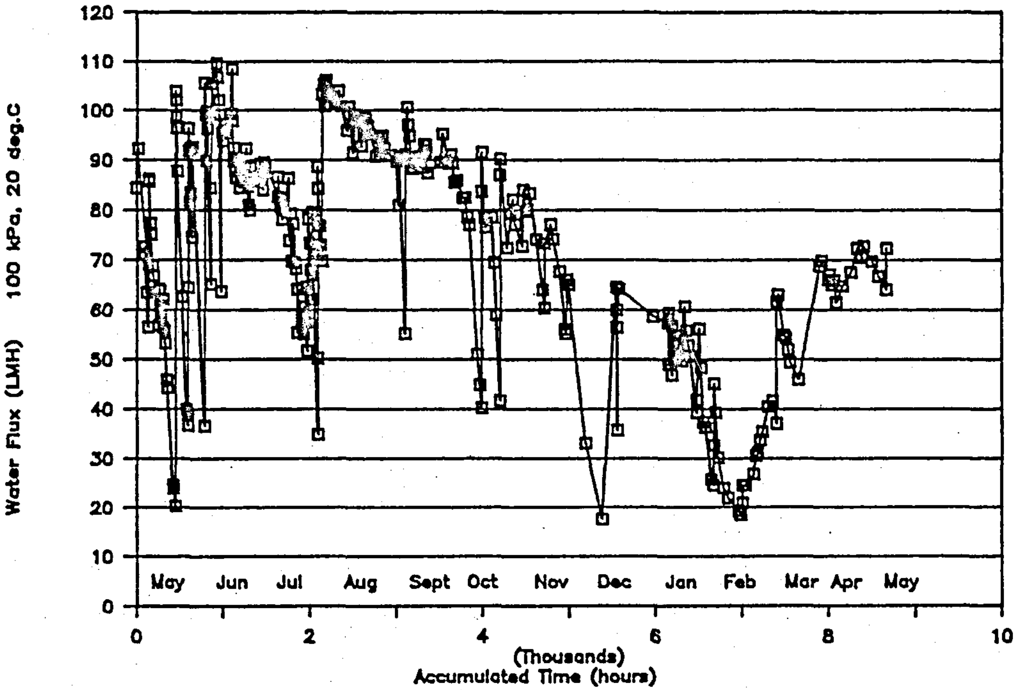
In order to curtail operating costs it was decided to keep the usage of detergents and cleaning chemicals to a minimum and preferably to eliminate them completely. During the study it was found that the introduction of air bubbles into the system successfully removed the fouling layer and restored flux values to their original. A brown silt, composed mainly of organic solid material, was flushed from the system during purging. A purging cycle entailed shutting off the system and allowing it to stand for 5 minutes followed by re-starting. The resultant shock wave effectively removed the fouling layer without the use of cleaning chemicals. It was found that the 5-minute standing period served to relax and detach the fouling layer which aided flux restoration on subsequent system start-up. The membrane showed no affinity for the fouling agents present in Paarl tap water and at the time of writing the membranes had operated continuously for 10 000 hours producing permeate of good quality. Flux values were maintained at approximately 85 $\ell m^{-2}h^{-1}$ using moderate operating conditions without the need for extensive chemical cleaning, except for flushing of the system with a 50 ppm chlorine solution at a frequency of about 1 000 hours to remove slime which resulted in a severe flux decline.

FIGURE 7.2
Illustration of 3 module UF cascade system



FI flow indicator
PI pressure indicator
TI temperature indicator
LC level control
BPCV back pressure control valve

FIGURE 7.3
Flux decline for cascade system on tap water



7.2.1.4 *Automation of operation*

The three-module cascade system was operated continuously without supervision and controlled by an automatic level control on the permeate tank. The simple control system consisted of two level-switches in the permeate tank, acting on a solenoid valve on the feed line. When the liquid level in the permeate tank reached the high level switch, the solenoid valve closed, shutting off the water supply to the system. Continued withdrawal of permeate from the tank caused the level to drop and upon reaching the low level switch resulted in the solenoid valve on the feed line to open. The system was set to deliver a constant permeate flow. On/off cycle times were adjusted by varying the draw-off rate of permeate from the balance tank.

7.2.1.5 *Economical operating parameters*

The UF membrane shows a high flux for relatively clean water such as tap water and the operating conditions for this type of application are relatively mild.

Although feed temperature has a very pronounced effect on flux values, the system was operated at ambient temperature in order to reduce operating cost to the bare minimum. Generally, unless an unused source of waste energy is available, heating of the feed stream to the system should not be considered.

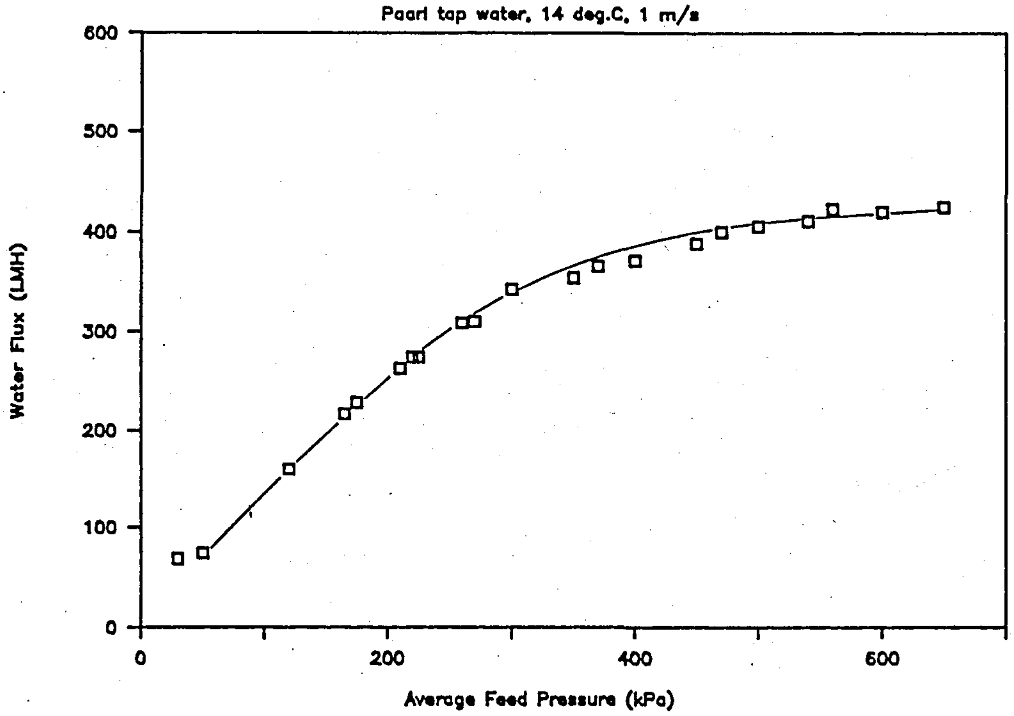
Even if such an energy source is available, the required additional capital outlay for heat-exchanging equipment would make the effort of producing an UF system that is able to compete with traditional filters in terms of cost and product quality, futile. In other words the gain in flux by heating of the feed stream is not deemed to be economical. Of course every application will have to be treated on merit. If, for instance, the permeate is used to produce a high-value end product, additional capital and operating cost might be justified.

Operating pressure, on the other hand (at ambient temperature), is also limited to approximately 500 kPa. Any further increase in feed pressure does not serve to increase flux rates since the flux/pressure curve nears an asymptote of 400 $\ell m^{-2}h^{-1}$ at approximately 500 kPa, which corresponds to the intrinsic water flux value for the particular membrane and application at the feed temperature used in the experiment (FIGURE 7.4). Since most water mains can deliver feed at a pressure of at least 600 kPa, attaining the maximum feed pressure of 500 kPa does not pose a problem.

Other operating variables to be considered are volume recovery and linear flow velocity. For large systems it is advantegeous to operate at low flow velocities to reduce system pressure-drop since the maximum usable pressure is only 400 kPa if a feed pressure of 450 kPa and an outlet pressure of 50 kPa are assumed. The three-module system (illustrated in FIGURE 7.2) was operated successfully at flow velocities as low as 0,5 m s^{-1}, and 1,0 m s^{-1} should be regarded as the upper limit to prevent excessive pressure losses. At a linear flow velocity of 0,5 m s^{-1} the pressure drop per series-connected module section was approximately 28 kPa at an average feed temperature of 16,6 °C and increased by roughly 6 kPa per series section for every 0,1 m s^{-1} increase in velocity. A feed flow velocity of 1 m s^{-1} would limit the amount of series-connected sections to about seven, when an allowable total system pressure drop of 400 kPa and average flux of 85 $\ell m^{-2}h^{-1}$ is assumed. System pressure drop is strongly dependent on flux, especially at high flux values when a great deal of pressure is lost purely due to flux through the membrane. The pressure drop values quoted above are valid only for a flux rate of 85 ℓ$m^{-2}h^{-1}$. The number of modules connected in parallel per series section (stage) is limited only by the available feed flow rate.

The effect of volume recovery on flux rate would not seem very drastic, nevertheless the general trend was found to be that an increase in recovery led to decreased, but stable flux. At 75% volume recovery flux rates were maintained in the proximity of the corrected value of 85 ℓ$m^{-2}h^{-1}$.

FIGURE 7.4
Flux *vs.* pressure for tap water



7.2.1.6 *System cost*

The capital cost for an ultrafiltration system described in the previous paragraphs is mainly attributed to module cost. As such, an investigation was made to reduce module cost while maintaining the basic support system.

In this investigation the module was assumed to consist of interlocking polypropylene rings housing 19 tubes, each having a diameter of 12,7 mm. These rings would simultaneously serve as a membrane support and a permeate collection vessel. Total module manufacturing cost including membrane tubes and end connections was estimated at R190. Since each module would have an effective membrane area of two square meters, this equates to a cost of R95 per m^2. Assuming a flux rate of 85 $\ell m^{-2}h^{-1}$, the manufacturing cost for a 100 m^3day^{-1} system, including plumbing, automation and instrumentation, was calculated as R60 per m^3 product. This translates to between R120 and R150 per m^3 product installed cost, depending on the amount of profit taken. Module cost amounts to about 80% of total capital cost for a system of this size and design type shown in FIGURE 7.2. Under the moderate operating conditions the UF modules are estimated to have a minimum life time of 5 years. This translates to an annual cost of about 8% of initial capital cost per anum for membrane replacement or 3,3 cents per m^3 product per year.

Direct operating cost in terms of cleaning chemicals is very low and electricity consumption is nil, with membrane replacement cost being the only indirect operating cost. Total cost per m^3 product depends strongly on the flux rate through the UF membrane and cost calculations indicated that the UF system could compete favourably with standard filters if high membrane flux rates could be maintained. A cost comparison between an ultrafiltration system of this type and a conventional in-line filter cartridge system is given in TABLE 7.1.

It follows that ultrafiltration becomes competitive at high flux rates due to the low operating cost associated with the system. For this type of application, the assumed membrane lifetime of 5 years is conservative and could be considerably longer in practice, which would reduce operating cost still further.

TABLE 7.1 COST COMPARISON BETWEEN CARTRIDGE FILTER AND ULTRAFILTRATION FOR THE CLARIFICATION OF TAP WATER

Assumptions:

Amortisation time 5 years,straight line depreciation
Running time 24 hours per day, 365 days per year
System size 100 m^3day^{-1}
Only cartridge/module cost considered,
cost of rest of supporting system and
plumbing, taken as identical

OPERATING/FILTER REPLACEMENT COST

	CARTRIDGE	MEMTUF (85 $\ell m^{-2}h^{-1}$)	MEMTUF (250 $\ell m^{-2}h^{-1}$)
flux (ℓ h^{-1})	1 500	170	500
lifetime (years)	0,5	5	5
total output per lifetime (m^3)	6 570	7 446	21 900
replacement cost (R)	300	300	300
cost per m^3 product (c/m^3)	4,57	4,03	1,37

The six-month life of the cartridge filter was obtained under actual operating conditions.

CAPITAL/FILTER COST

	CARTRIDGE (0,2 μm)	MEMTUF (85 $\ell m^{-2}h^{-1}$)	MEMTUF (250 $\ell m^{-2}h^{-1}$)
flux (ℓ h^{-1})	1 500	170	500
no. of modules	2,78	24,51	8,33
cost per module (R)	800	610	610
module cost (R)	2 224	14 951	5 081
permeate removed (m^3)	182 500	182 500	182 500
cost per m^3 product (c/m^3)	1,22	8,00	2,78
total cost (c/m^3)	5,79	12,03	4,15

7.2.1.7 *Conclusions*

The quality of UF permeate obtained from tap water as the feed scource, is excellent and generally superior to that obtained from a 0,2 μm filter. The analytical results of raw Paarl tap water and UF permeate as determined by the water analysis department of the Bellville branch of the CSIR, are given in TABLE 7.2.

TABLE 7.2 ANALYTICAL RESULTS OF CATRIDGE FILTRATE AND ULTRAFILTRATION PERMEATE OBTAINED FROM TAP WATER FEED

	PAARL TAP WATER		UF PERMEATE
	raw	after 0,2 μm Millipore filter	
Turbidity (NTU)	0,96		0,05
Colour (Mazen units)	10	< 5	< 5
Suspended Solids (mg ℓ^{-1})	1,90		0,50
COD (mg ℓ^{-1})	5	< 5	< 5
pH	8,60		8,50
Conductivity (mS/m @ 25 °C)	8,80		8,90
Silica as Si (mg ℓ^{-1})		1,44	1,43
Phosphate as P (mg ℓ^{-1})		0,05	0,08
Calcium as Ca (mg ℓ^{-1})		12,80	12,80
Magnesium as Mg (mg ℓ^{-1})		0,70	0,6
Iron as Fe (mg ℓ^{-1})	0,083	< 0,025	< 0,025
Manganese as Mn (mg ℓ^{-1})	0,075	< 0,025	< 0,025
Absorption (4 cm)			
545 nm	0,011	0,000	0,000
275 nm	0,075	0,043	0,031
254 nm	0,092	0,059	0,046

It can be seen that the permeate had excellent clarity, low suspended solids and, interestingly enough, most of iron and manganese was removed by the UF step. Futhermore from the cost calculations of the previous paragraph it follows that UF can be competitive in terms of operating cost with cartridge filters at high flux rates.

7.3 FOOD APPLICATIONS

Ultrafiltration in the food industry is chiefly concerned with clarification, concentration or stabilisation of some intermediate raw material in order to obtain a valuable nutritious end-product. With regard to concentration, UF competes directly with evaporation, even more so when thermally sensitive substances have to be processed. Since UF does not involve a phase change, dewatering of heat-sensitive materials is achieved without chemically altering the particular product.

Where products have to be clarified or stabilised prior to storage or packaging, UF can in most cases replace traditional bentonite/gelatine fining and sheet filtration since these processes are very labour-intensive and consume vast amounts of fining chemicals and filtration aids.

This section deals with how the UF system operated in selected, established application fields in the food industry.

7.3.1 BEVERAGE INDUSTRY

In the preparation of fruit juices, UF is used for the simultaneous clarification of and stabilisation of protein in the raw juice to give it an extended shelf life. The fruit juices studied during bench and trial runs were apple, pear and grape juices.

Traditional methods of fruit juice clarification involve several batch operation steps (refer to FIGURE 7.5) such as

(i) enzymatic hydrolysis of cloud stabilising polysaccharides;
(ii) addition of chemical coagulants and fining agents;
(iii) centrifugation and diatomaceous earth filtration.

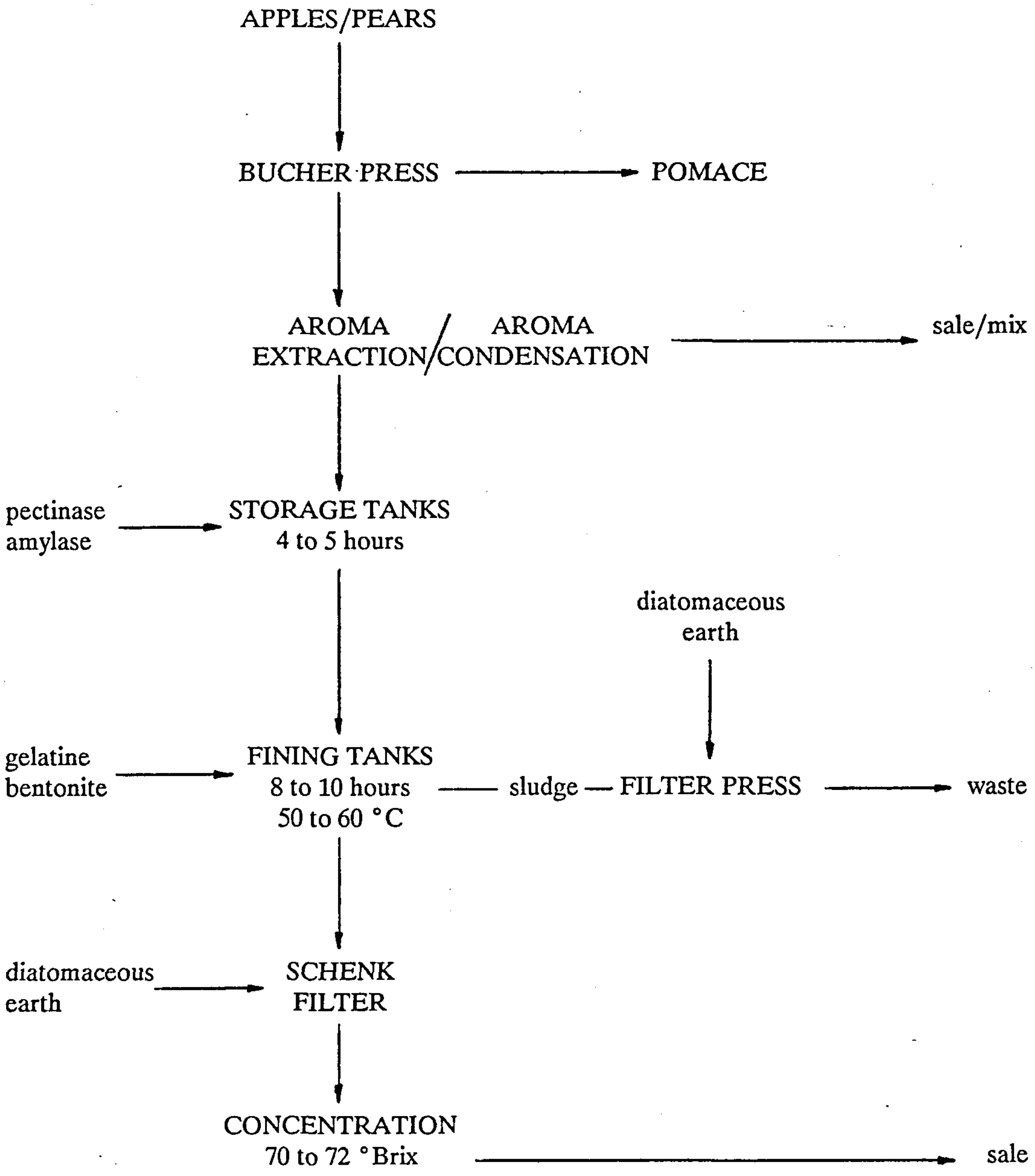
These methods are labour-intensive, time-consuming and involve the use of large fining (settling) tanks. They also do not always fully achieve their purpose. Ultrafiltration can clarify and stabilise fruit juice in a single operation. The process has been applied commercially with success and is reported to have improved the economics of juice clarification *(Breslau et al., 1984).*

7.3.1.1 *Apple and pear juice*

During the 1986 season a on site bench study was performed at Ceres Fruit Growers, Ceres on the clarification of apple juice by ultrafiltration. Initial results looked promising especially with regard to juice quality and this investigation paved the way for subsequent full-scale pilot studies on apple and pear juice clarification during the 1987 season. During that time the possibility of reclaiming extra juice from fining tank sludge was also investigated.

FIGURE 7.5

Process flow diagram for the traditional method of fruit juice clarification



7.3.1.1.1 *Materials and methods*

Apple and pear juice was obtained from the juice plant directly after aroma extraction and prior to bentonite and gelatine/enzyme addition. A process flow diagram of the traditional clarification method is given in FIGURE 7.5. The juice was of the so-called press type (Bucher press) and had a typical temperature of 55 to 60 °C. This juice was subjected to UF in a batchwise manner and concentrated to between 90 and 95% by volume in a matter of six to ten hours to simulate full-scale production conditions. Batch sizes for the bench plant ranged from 350 ℓ to 550 ℓ and between 3 000 ℓ to 5 000 ℓ for the pilot plant. Total membrane area for the bench and pilot plants were 4 m^2 and 20 m^2 respectively. Typical operating conditions were 50 to 60 °C feed temperature and a feed pressure of 600 kPa. Linear flow velocity inside the tubes was kept constant at 2 m s^{-1}. Permeate samples were taken at regular intervals and analysed by the Ceres Fruit Growers (CFG) laboratory for clarity, haze, colour, protein stability as well as pectin and starch contents. The membranes used in the trial had an approximate molecular mass cut-off (MMCO) of 40 000 as determined by the standard test method.

7.3.1.1.2 *Effect of feed temperature on flux*

The effect of feed temperature on the permeation rate of the UF membranes was investigated by operating the system in total recycle mode. Flux rates increased linearly with an increase in temperature due to decreasing viscosity of the feed solution. Feed pressure was kept constant at 600 kPa. Results are illustrated in FIGURE 7.6. It was therefore obvious that a production system should be operated at the highest allowable temperature. Since the membrane system can tolerate up to 70 °C, the obvious choice for feed temperature was between 50 and 60 °C, which is the typical aroma-plant outlet temperature.

7.3.1.1.3 *Flux decline during recovery*

When permeate was collected and not returned to the feed tank, the feed stream was concentrated as the juice was processed. This increase in concentration or volume recovery of permeate reduced the permeate flux. The effect is shown in FIGURE 7.7 and indicates that the decline curve follows an exponential relationship for both apple and pear juice.

The curve is of the form

$$y = a\ exp\ (bx)$$

where

x = %volume recovery
y = flux value (ℓm^{-2}h^{-1})
a and b are experimentally determined constants

In general the fit of this type of curve to the typical data points of FIGURE 7.7 is good. Regression analysis gave the following values:

apple juice

regression coefficient	$R^2 = 0{,}933$
intercept	$a = 33{,}0\ \ell m^{-2}h^{-1}$
slope	$b = -0{,}0113$ LMH/%

pear juice

regression coefficient	$R^2 = 0{,}998$
intercept	$a = 54{,}72\ \ell m^{-2}h^{-1}$
slope	$b = -0{,}0346$ LMH/%

The flux decline for pear juice was found to be more pronounced than that for apple juice. This can possibly be attributed to the high feed pressure (600 kPa) used during the experiment. This point is discussed in more detail in the next paragraph. Unfortunately the experiment could not be repeated due to the unavailability of pear juice at the time.

The flux decline curve was not found to fit the relationship

$$y = a - b(\ln x)$$

very well, where

x = volume concentration ratio
y = flux value
a and b experimental constants

This relationship was formulated by *Heatherbell (1977)* for apple juice and found to apply to pear juice as well by *Kirk et al. (1983)*.

The obvious discrepancy between experimental results and those in the literature can possibly be attributed to different membrane configuration (tubular instead of hollow fibre), but more likely to different preparation and pretreatment of the juice, prior to UF, or perhaps a difference in inherent fruit quality.

FIGURE 7.6
Effect of temperature on flux : apple juice

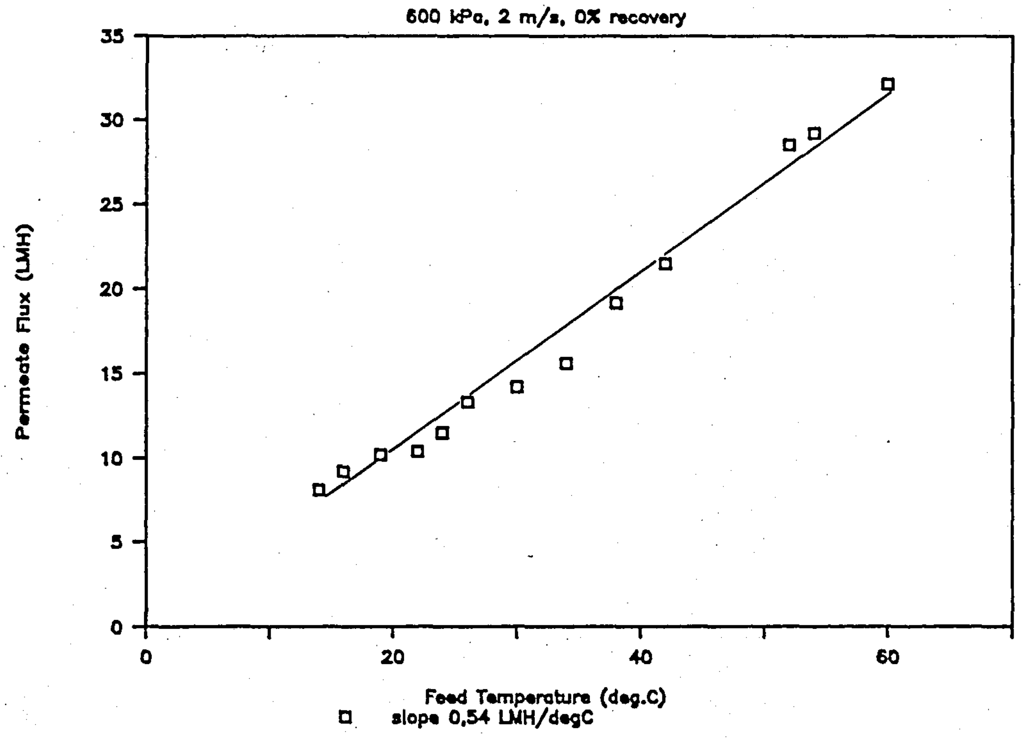
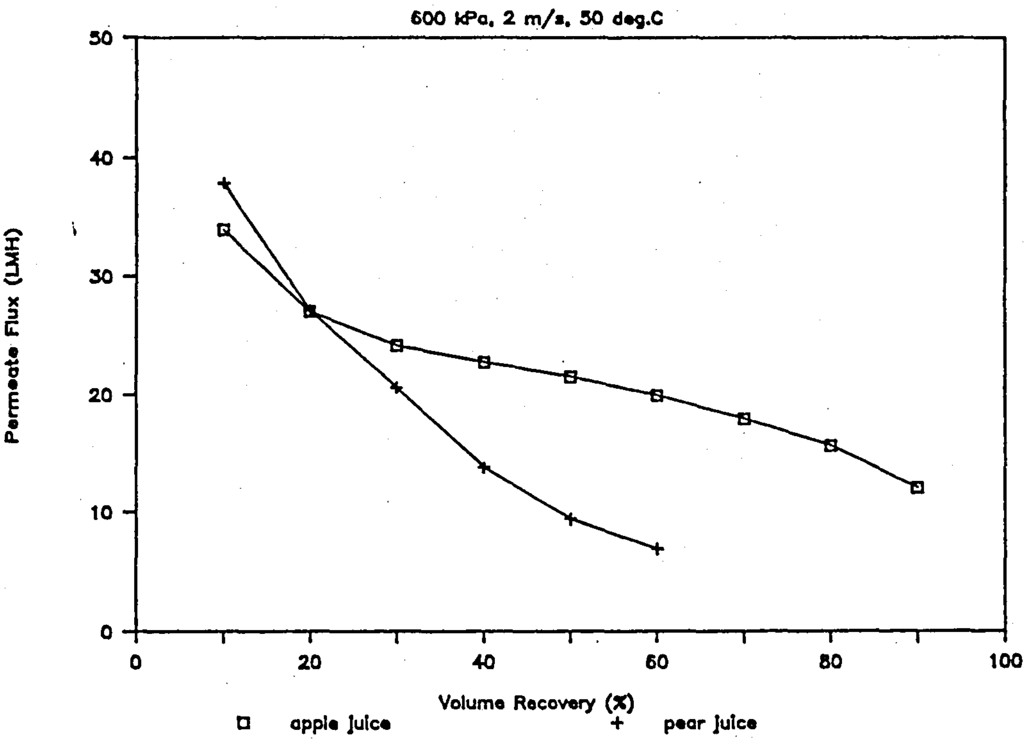


FIGURE 7.7
Flux decline curve during recovery : apple/pear juice



7.3.1.1.4 *Effect of feed pressure on flux*

Feed pressure was found to have a pronounced effect on the flux rate for raw, untreated apple juice. Generally, flux rates increased with increase in feed pressure. The increase in flux rate gained above a feed-pressure value of 600 kPa was practically negligible. Bench and pilot studies were therefore usually run at a feed pressure of 600 kPa and the feed temperature instead was raised by heating with steam whenever possible in order to maximise flux values. In the case of pear juice, however, *Kirk et al. (1983)* reports that the filtration rate is strongly dependent on feed pressure. Flux rates dropped markedly when the optimum feed pressure value was exceeded. The reason for this phenomenon lies in the physical nature of pear juice. Pectic substances in pear juice supposedly cause the build-up of a gel layer on the membrane surface. According to *Doesburg (1965)* and *Pilnik and Voragen (1970)*, these pectic substances are chain-like combinations of galacturonic acid units aggregated by hydrogen bond bridges. When the gel layer is compressed by excessive feed pressure, these bridges could collapse and the network of chains closes off the membrane, according to *Kirk et al. (1983)*. As mentioned in the previous paragraph, this phenomenon could unfortunately not be studied in more detail due to the unavailability of pear juice at the time of the trials.

7.3.1.1.5 *Juice quality*

Point samples at various stages during the recovery cycle as well as composite samples at the end of the concentration cycle were taken of both apple and pear juice permeate. These samples were analysed by the Ceres Fruit Growers (CFG) laboratory for clarity, haze, colour, stability and the presence of pectin and starch. Consistent high-quality values were obtained throughout the three-week trial period. When compared with the quality of juice obtained by the traditional fining process, the UF permeate was found to be superior overall, but especially with respect to clarity and stability. UF permeate samples showed positive stability and negative starch and pectin contents at all times. Colour variations were negligible throughout the concentration cycle. A comparison between typical UF permeate and traditionally fined juice analysis results is given below.

	APPLE		PEAR	
	UF	CFG Spec.	UF	CFG Spec.
Clarity (%) @ 625 nm	98-100	>90	97-99	>90
Haze (NTU)	0,1-1,2	<6,0	0,2-1,3	<6,0
Colour (%) @ 440 nm	50-75	>50	60-70	>50
Stability	pos	pos	pos	pos
Pectin	neg	neg	neg	neg
Starch	neg	neg	neg	neg

7.3.1.1.6 *System cleaning*

The fouling of membranes and the corresponding decline in flux rates, is a well established fact *(Robertson, 1984)*. In order to maintain flux values at an acceptable level, ultrafiltration membranes have to be cleaned regularly. It was found that when treating juice on consecutive days without intermittent cleaning, a serious decline in flux rates resulted. A flux reduction of up to 40% in mean flux was experienced. More important, however, was the fact that the flux decline rate during the recovery cycle on the second day was always more pronounced, and treating the same volume of juice took considerably longer than on the first day. Systems were therefore cleaned regularly, normally at the end of the concentration cycle.

In order to observe the effect of cleaning procedures on flux restoration, the water flux values were noted after each cleaning cycle. The results are shown in FIGURE 7.8. A 0,5% solution of sodium lauryl sulphate (SLS), corrected to pH 11 with sodium hydroxide (NaOH), was used in a 45-minute washing cycle at 20 °C and resulted in complete restoration of water flux values to their original. The washing cycle could be shortened considerably, if required, by using a hot (40 to 50 °C) cleaning solution. After the cleaning-in-place (CIP) procedure, the system was flushed with good quality water, preferably at elevated temperature, to remove all traces of cleaning chemicals.

7.3.1.1.7 *Comparative run against Abcor™ system*

Experimental UF membranes of 40 000 MMCO (type 719) were evaluated against ABCOR™ 18 000 MMCO membranes in the clarification of apple juice. Both systems were subjected to identical operating conditions *i.e.* the systems were run side by side.

Experimental: The MEMTUF 20 pilot plant (FIGURE 7.9) with 20 m^2 membrane area was operated in parallel with the Appletiser™ UF plant at Grabouw, on a mixed variety apple juice. The Appletiser™ plant utilised ABCOR™ HFM-163 membranes and had a total membrane area of 235 m^2. The juice was of the diffusor type and had negative pectin and starch values. Readings on both plants were taken simultaneously at half-hourly intervals.

Operating Conditions: Every endeavour was made to subject both plants to identical operating conditions. The feed temperature was 55 °C and the feed pressure was 540 kPa. These conditions were regarded as optimum for the operation of the ABCOR™ plant. Outlet pressure for the MEMTUF 20 plant was 450 kPa and that for the ABCOR™ plant was 270 kPa.

Flux rate: It would seem that under identical conditions the flux rate for the type 719 membrane is roughly half that for the ABCOR™ HFM-163 membrane on diffusor type apple juice. However, the 719 membrane is by no means an optimum membrane in terms of flux for apple juice treatment. In the case of the ABCOR™ system it can be assumed with some certainty that the membrane as well as the operating conditions were optimised for this particular application (see FIGURE 7.10 for a flux rate comparison).

Product quality: The quality of the permeate from the MEMTUF plant was on a par (slightly better in fact) with that of the ABCOR™ plant. Permeate from the MEMTUF unit had an average transmittance of 97,0% at 625 nm, while that for the ABCOR™ plant was 96,2% on average. Higher transmittance indicates higher quality. This experiment illustrated once more that MMCO cannot be used as an absolute measure to predict membrane performance. Although the membranes had a dissimilar MMCO value as per definition, they gave virtually identical juice (permeate) quality.

Conclusions: It is felt that after some optimisation of membrane characteristics and operating conditions for the particular application, flux rates could be improved considerably. At present, however, the MEMTUF system can still compete favourably in terms of capital cost with other imported UF systems, despite requiring double the membrane area.

FIGURE 7.8
Effect of cleaners on flux restoration after membrane fouling : apple/pear juice

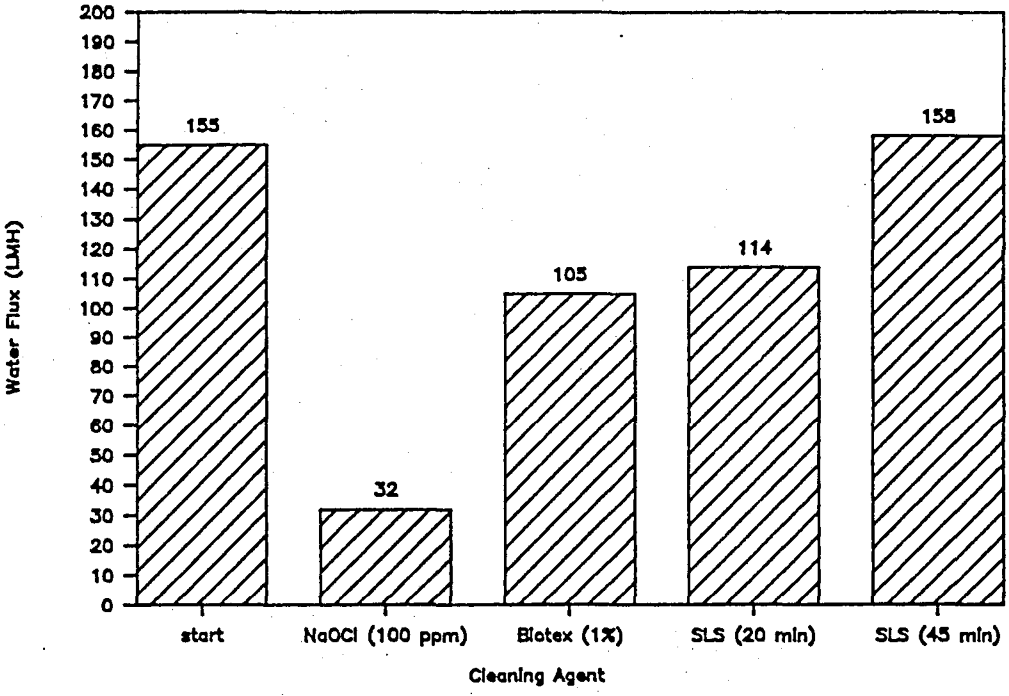
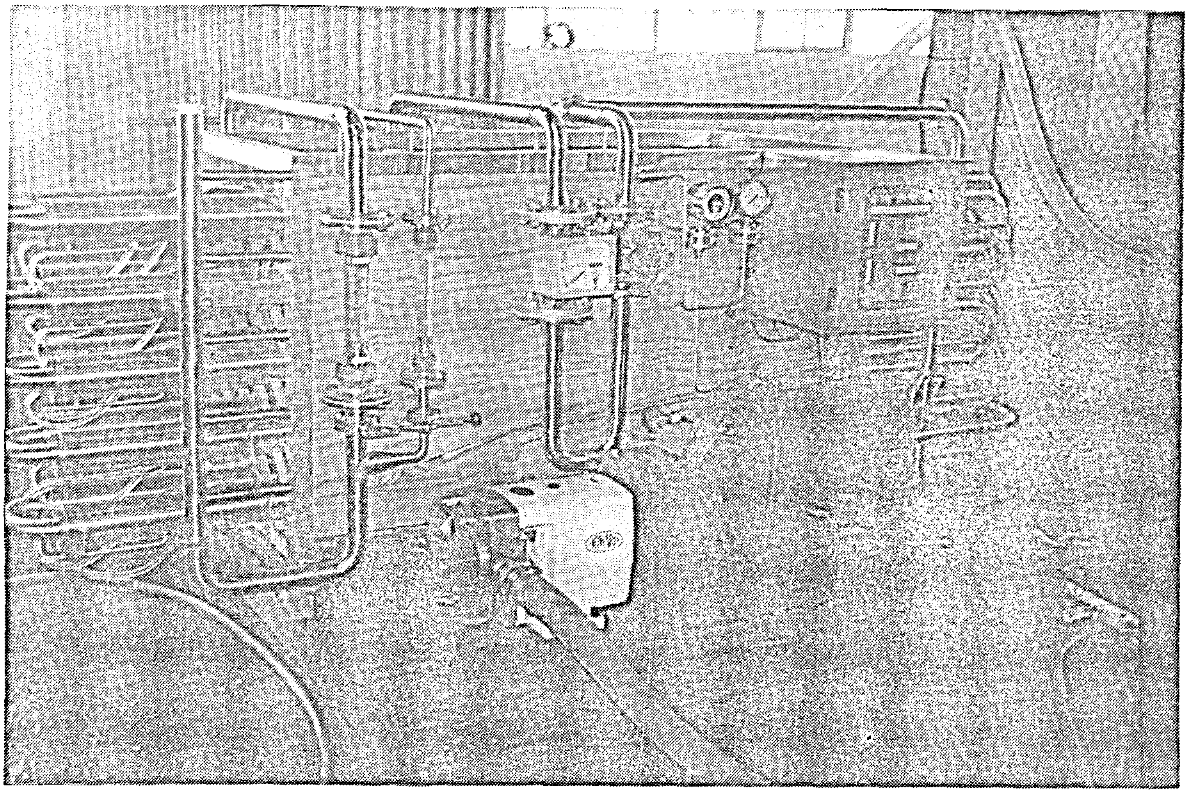
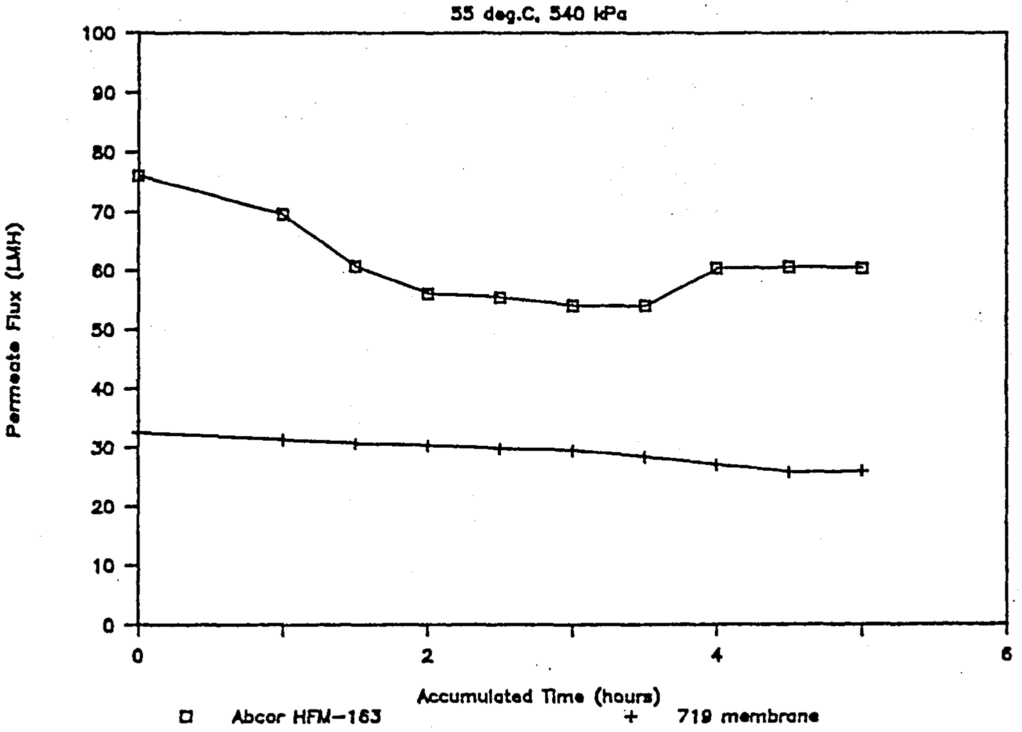


FIGURE 7.9
MEMTUF 20 pilot plant



Photograph of the MEMTUF 20 food grade UF pilot plant fitted with a series train of 10 modules (20 m^2 membrane area) of parallel tube configuration. This plant was used for fruit juice and sludge clarification experiments as well as for the clarification of tap water at the polystyrene plant.

FIGURE 7.10
Abcor™/Memtuf flux comparison : apple juice



7.3.1.2 Apple and pear sludge

Apple and pear sludges were treated with the MEMTUF 20 pilot unit, using modules with a parallel tube configuration.

Sludge was obtained from the fining tank after the normal clarification process (enzyme and bentonite/gelatine addition) had been completed.

The UF System was operated in a batch mode with internal recirculation. In other words, a feed stream was taken off the feed tank and pumped through the UF plant. The concentrated outlet stream from the plant was recirculated to the feed tank while permeate was drawn off continuously.

Feed pressure ranged from 200 to 500 kPa and feed temperature varied from 51 to 69 °C. Permeate and concentrate samples were taken at regular intervals throughout the concentration cycle. The samples were analysed by the CFG laboratory for sugar content (°Brix), clarity, colour, haze, total solids and stability.

7.3.1.2.1 *Volume recovery*

The maximum attainable volume recovery based on economical flux value considerations, was found to be between 75 and 85% depending on the solids concentration of the original feed. When the starting solids concentration was 15% or higher, a volume recovery of 75% resulted in a concentrate which contained 80 to 90% solids. With an original solids concentration of 10% or lower, a volume recovery of 85 to 90% could beobtained.

7.3.1.2.2 *Flux values and flux decline during recovery*

Average flux values for apple sludge were 60 $\ell m^{-2}h^{-1}$ at 65 °C and 250 kPa. Under identical operating conditions (pressure, temperature, % solids in feed), the flux values for pear and apple sludges were found to be similar. Charcoal is sometimes added to the fining tank to speed up the clarification process when overripe fruit is treated. Addition of charcoal to the sludge had a detrimental effect on flux values due to the increase in solids resulting from this action. A typical flux decline curve during the recovery cycle is shown in FIGURE 7.11 for apple sludge. Flux rates for pear sludge under identical operating conditions were similar. The curve has a flat profile, but after 60% volume recovery, which corresponds to a solids concentration of 25 to 30% in the feed stream, there was a sharp decline in flux. Addition of charcoal to the sludge prior to UF resulted in lower flux values since the solids content of the feed was increased. Sludge to be processed by UF should therefore be drawn directly off the bottom of the fining tank without any additional treatment.

7.3.1.2.3 *Pressure drop*

A typical system pressure-drop curve is shown in FIGURE 7.12. The steep increase in pressure drop corresponds to the rapid increase in solids towards the end of the concentration cycle. The curve shows the total pressure drop accross a series train of 10 modules with parallel tube configuration.

FIGURE 7.11
Flux decline curve during recovery : apple sludge

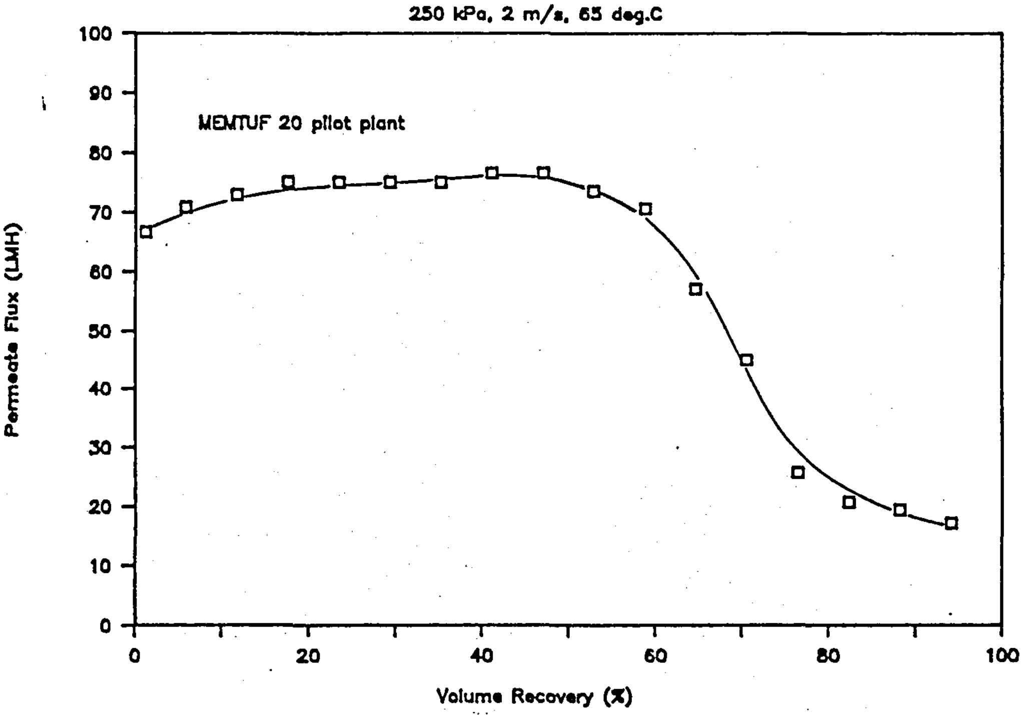
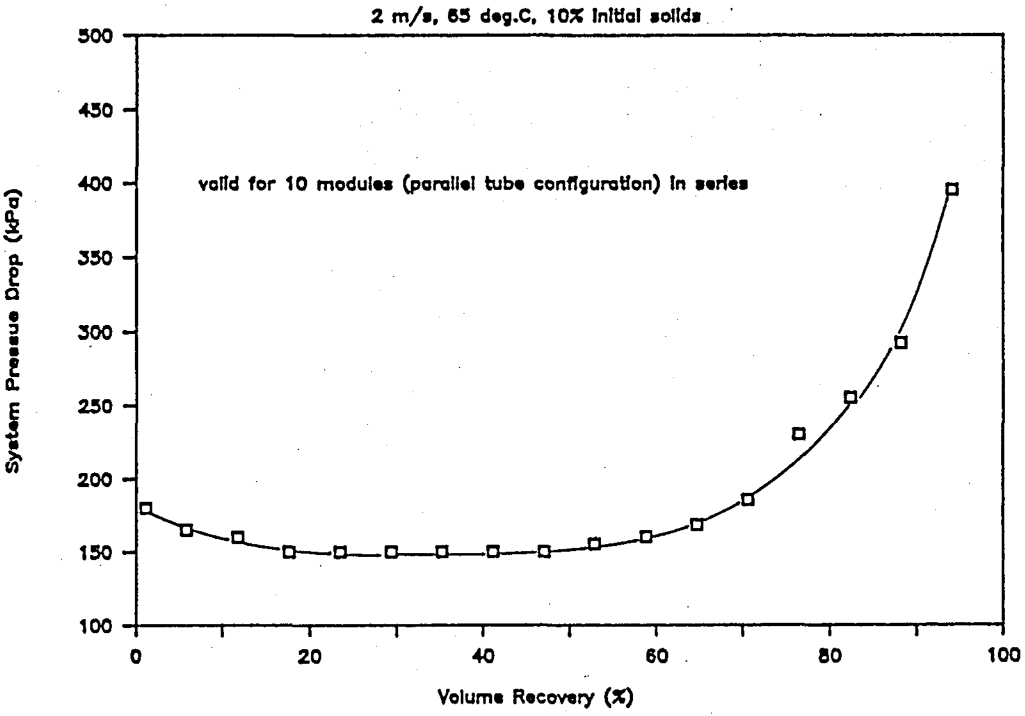


FIGURE 7.12
System pressure drop during recovery : apple sludge



7.3.1.2.4 *Diafiltration*

The use of diafiltration towards the end of the concentration cycle did not result in the expected high gain of flux values, but could be considered should it be neccessary to reclaim as much sugar as possible.

7.3.1.2.5 *System cleaning*

In order to maintain high flux values, proper cleaning of the UF system was essential. After each concentration cycle the system was flushed immediately with hot water at 45 to 50 °C in order to remove the paste-like, concentrated sludge. When the system was allowed to stand with sludge in the flow channels of the membrane modules, blockage occurred upon cooling. Although the method was tedious, blocked modules could be cleared by flushing individual tubes with a water jet. A daily caustic wash at pH 11, combined with chlorine sterilisation (200 ppm) was essential to maintain flux values at a constant level.

7.3.1.2.6 *Conclusions*

Samples of permeate and concentrate were taken during the concentration cycle. The permeate resulted in a stable, clear juice in both apple and pear sludge. Sugar content (reflected by °Brix) of the permeate remained constant throughout the concentration cycle; in other words, no additional sugar was lost to the concentrate. Clarity and haze values were excellent. Analysis results for clarified apple and pear sludge are shown in TABLES 7.3 and 7.4

TABLE 7.3 APPLE SLUDGE SAMPLE ANALYSIS RESULTS

PERMEATE						SLUDGE	
Volume recovery (%)		°Brix	Clarity @625 nm (%)	Colour @440 nm (%)	Haze (NTU)	% Solids	°Brix
17,7		13,4	97	70	0,2	8	13,7
29,4		13,1	96	72	0,1	10	13,2
41,2		13,3	96	70	0,1	18	13,7
52,9	cold	13,1	98	71	0,2	20	13,1
	hot		97	69	0,4		
64,7		13,5	99	76	0,2	25	13,5
70,6						40	13,4
76,5		13,2	99	75	0,3	55	13,4
82,4						60	14,1
88,2		13,3	100	76	0,9		
94,0	cold	13,5	99	74	0,3	70	13,9
	hot		99	73	0,6		

The permeate sample at 94% recovery was a composite sample *i.e.* a representative sample of permeate during the whole concentration cycle.

TABLE 7.4 PEAR SLUDGE SAMPLE ANALYSIS RESULTS

PERMEATE						SLUDGE	
Volume recovery (%)		°Brix	Clarity @625 nm (%)	Colour @440 nm (%)	Haze (NTU)	% Solids	°Brix
0		12,9	99	96	0,3	12	13,5
8,3		13,2	100	97	0,2		
16,7		13,2	100	97	0,4		
25,0	cold	13,3	100	98	0,2		
	hot		98		0,5		
33,3		13,3	100	97	0,1		
41,6		13,8	100	98	0,1		
50,0		13,3	100	97	0,1		
58,3		13,5	100	97	0,2		
66,7		13,4	100	98	0,1		
75,0	cold	13,5	100	98	0,1	80	13,3
	hot		99		0,4		

Permeate sample at 75% recovery was a composite sample.

The studies showed that the ultrafiltration of fruit juice sludge resulted in an end-product of superior quality when compared to the traditional method, at what can be considered to be economical flux values. A cost comparison between the traditional processing method and ultrafiltration for this application is given in CHAPTER EIGHT section 8.2.2.

7.3.1.3 *Guava sludge*

The filtration of guava sludge (after fining) by filter press and alluvial filter was found to give rise to problems by a producer of fruit juice products. This was mainly due to the high volume of sludge formed in the processing of the fruit. Because of the high cellular content of guava juice, roughly double the amount of sludge is formed during the normal fining process when compared with apple juice. Filtration rates for the filter press were found to be low and the quality of the end product was generally poor and inconsistent.

During a bench study on-site, ultrafiltration of the sludge proved to yield a product of much improved quality at flux rates ranging from 25 to 46 $\ell m^{-2}h^{-1}$ during the concentration cycle, at a feed temperature of 42 °C. Sludge obtained after the normal fining process at 10% solids content and was concentrated to 85% recovery by volume to a final concentrate containing 95% solids. The permeate (clarified guava juice) was of excellent quality and suitable for the production of guava juice concentrate. A composite permeate sample showed a transmission of 97% at 625 nm compared to the 79% of the sample from the existing sludge filter. Final sludge volume was reduced to about 20% of the original volume.

7.3.1.4 Grape juice

The wine industry showed interest in the possible use of UF in the wine making-process after a reverse osmosis plant for simultaneous tartrate/protein stabilisation had been installed.

The objective was to determine wether UF could be utilised to stabilise grape juice. This proved to be the case after several bench runs had been conducted at Stellenbosch Farmers Winery (SFW) in Stellenbosch. The possible use of UF for must stabilisation was confirmed.

7.3.1.4.1 *Study results*

Two types of grape juice, otherwise referred to as must in the wine industry, were treated by UF, *viz* Clairette Blanche and Hanepoot. Of the two, Hanepoot must proved more difficult to treat, generally giving lower flux values than Clairette Blanche under identical operating conditions. This was attributed to the higher protein content of Hanepoot must. Membranes with a 40 000 MMCO gave a clear, protein stable permeate at all times. Coarser membranes of 60 000 MMCO, although yielding increased flux values, failed to produce a stable product. The juice (must) treated was of single strength, freshly pressed and free of additional enzymes. Feed analysis results showed the following typical values:

pH	3,1 - 3,3
Total acid	6,3 - 7,0
°Brix	20,0 - 22,5

The effect of feed temperature on membrane flux is illustrated in FIGURE 7.13. Flux was found to be a maximum at approximately 26 °C, dropping off sharply at higher temperatures. This fact was attributed to protein denaturation, resulting in membrane fouling. Subsequent tests were done at a feed temperature of not more than 20 °C. A lower feed temperature between 15 and 20 °C was preferred by the wine industry to prevent the possible loss of volatile and aromatic constituents at elevated temperatures.

7.3.1.4.2 *Feed pressure and flux values*

An increase in feed pressure resulted in an increase in membrane flux, as is generally the case. The effect of feed pressure on the permeation rate during the recovery cycle is shown in FIGURES 7.14 and 7.15, for Hanepoot and Clairette Blanche, respectively. The results showed that flux increase for Hanepoot was less pronounced than that for Clairette Blanche for an identical pressure increase, and that this flux increase became less pronounced at higher pressure values for both types of must. For Clairette Blanche, an increase in feed pressure from 400 kPa to 600 kPa resulted in a flux increase of approximately 58% while the increase for Hanepoot was roughly 52%. A feed-pressure increase from 600 kPa to 800 kPa resulted in a 30% flux increase for Clairette and a 25% increase in flux for Hanepoot. The maximum feed pressure for grape juice or must would thus seem to be in the region of 1 000 kPa. Any further increase above such a value would result only in a negligible flux increase.

7.3.1.4.3 *Permeate quality*

The permeate obtained during the studies was stable at all times, and no secondary haze formation occurred after the ultrafiltration step, when a 40 000 MMCO membrane was used. Membranes of 60 000 MMCO resulted in a 38% flux increase at identical operating conditions, but failed to produce a stable product. Haze values of the permeate ranged from 0,2 to 0,6 NTU and the difference between cold and hot haze measurements varied from 0 to 0,2 NTU. The permeate was thus considered to be extremely protein-stable. Must is considered unstable when the difference between the hot and cold haze measurements exceeds 3 NTU. The only objection from the wine industry to the UF process was the loss of some colour in the product. As such the industry foresaw that must treated by UF could be used only in the sweetening of lower quality wines. Taste was judged to be unaffected by the UF process.

7.3.1.4.4 *Membrane cleaning*

The proteins present in unfermented must tended to cause substantial membrane fouling and a daily washing routine had to be applied to maintain proper flux values. A variety of cleaning agents were tried during the tests, and a combination of NaOH and chlorine was found to be very effective in restoring flux values. This corresponds with a similar method cited in the literature *(Kuroda, 1986)*. The effects of various cleaners on the restoration of water flux is shown in FIGURE 7.16. A daily washing cycle of 15 minutes at 20 °C with 500 ppm NaOCl, corrected to pH 11 with NaOH, served to restore the water flux value of the membranes to the original.

7.3.1.4.5 *Conclusions*

The ability of UF to clarify and stabilise must and wine successfully was demonstrated by these trials. Since the wine industry is very seasonal in terms of labour intensity, UF could be a useful tool in processing the large volumes of must and wine during the short 3- to 4-month harvesting season, when consistent production rates of constant quality are required. This cannot always be achieved with the traditional fining methods. With some tailoring of membrane characteristics the problem of colour reduction of the must could possibly be overcome, which should make UF an attractive means for clarification and stabilisation in the wine industry.

FIGURE 7.13

Effect of feed temperature on flux : must

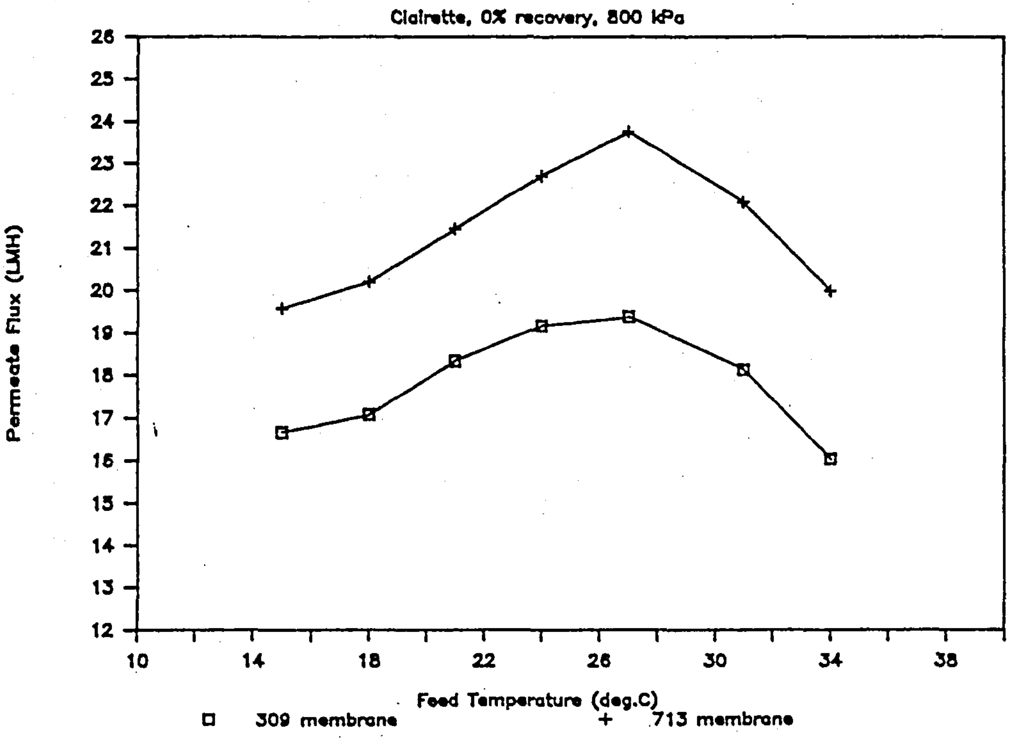


FIGURE 7.14

Effect of recovery on flux at various feed pressures : Hanepoot

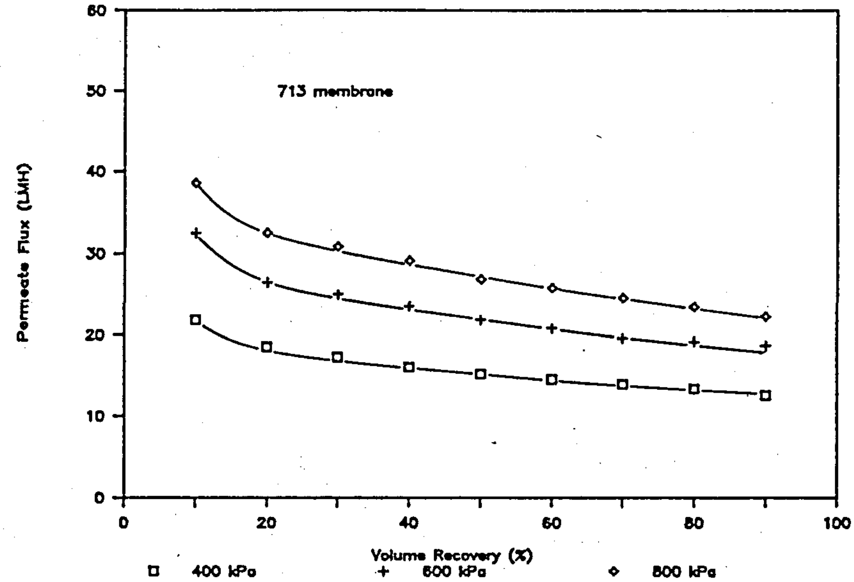


FIGURE 7.15

Effect of recovery on flux at various feed pressures : Clairette Blanche

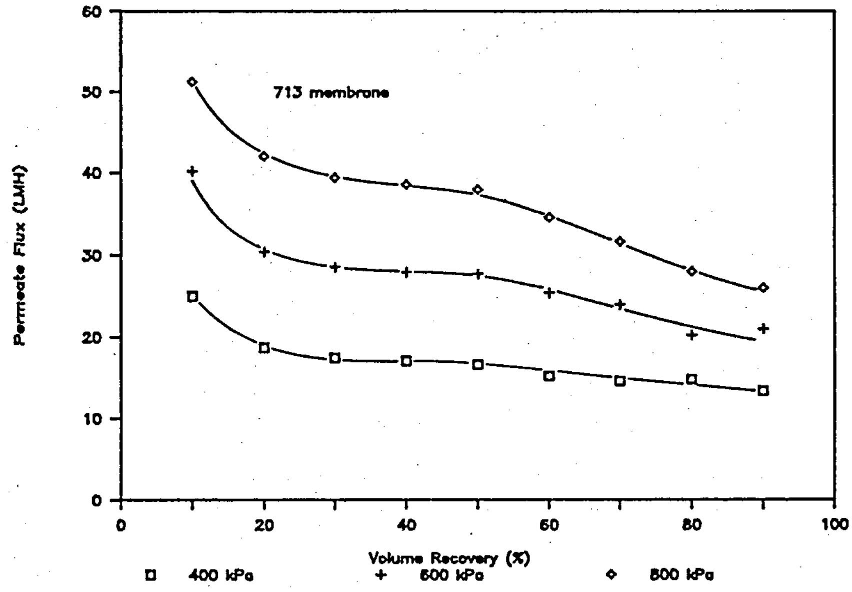
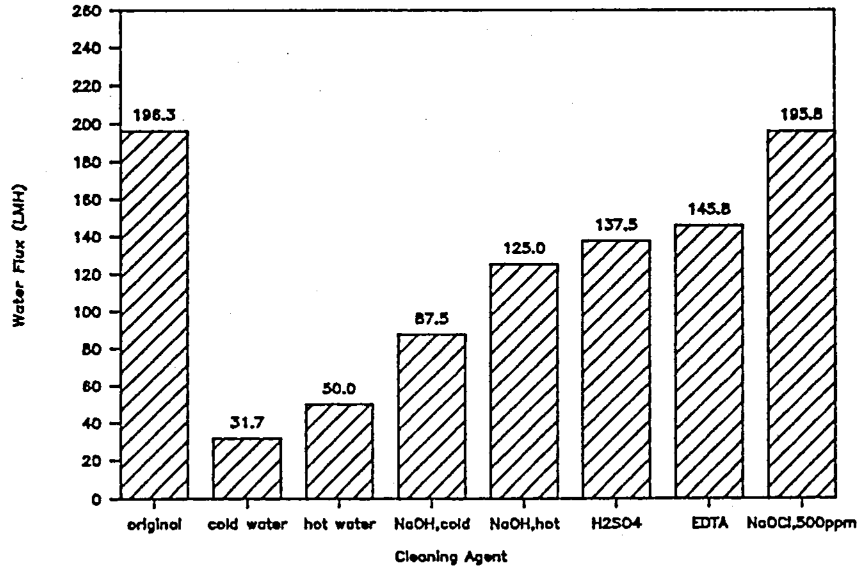


FIGURE 7.16

Effect of cleaners on flux restoration after membrane fouling : must



7.3.2 DAIRY INDUSTRY

In Europe and the United States of America, the largest membrane area in the food sector has been installed in the dairy industry *(Gekas et al., 1985)*. Ultrafiltration is being used mainly for the concentration of whey to produce whey protein concentrates (WPC) of different protein contents. To a lesser extent UF is used during cheese-making for the preconcentration of milk, giving added yield with respect to fats and proteins *(Hansen, 1977* and *Jacobsen, 1985)*. An excellent review article on the subject was published by *Matthews (1979)*.

In South Africa however, the dairy industry was found to be extremely committed to traditional ways of manufacture. As far as could be ascertained no UF equipment is being used commercially in the South African Dairy Industry. However, studies were recently carried out by T.E.H. Downes of the Animal and Dairy Science Research Institute, Irene, on the use of UF during Cheddar and Gouda production. He established that considerable savings could result from the use of UF in the production of hard cheeses. This was in accordance with the findings of *Glover (1985)* who reports substantial savings by the use of UF in the production of Feta, Mozarella, Queso fresco and cheese base. Unfortunately a complete revolution of the existing cheese-making process would be required and the South African dairy industry is not geared towards such a drastic change. This is mostly due to the large number of milk producers supplying relatively small volumes of dairy products. This situation is bound to change in the future with more and more small suppliers being incorporated into large dairy concerns. Once large volumes of milk are being processed at a single location, the use of membrane processes in the dairy industry could become the norm.

It was nevertheless decided to investigate how the experimental membranes performed on a traditional application in the dairy industry. Since large volumes of fresh milk were difficult to obtain, it was decided to run a bench study on cheese whey for the recovery of proteins. Whey is normally regarded as a useless byproduct during traditional cheese-making and as well as an effluent problem. The main object was to determine whether flux values and WPC quality similar to those reported in the literature could be obtained with locally manufactured membranes.

7.3.2.1 Study results

Cottage cheese and cheddar whey was concentrated using membranes with a 40 000 MMCO. Most proteins and fats were recovered while a substantial amount of lactose passed through the membrane. Sample analysis results as determined by the Dairy Section of Elsenburg Agricultural College, Stellenbosch, are shown below for Cheddar whey.

Sample	Fat % m/m	Protein % m/m	Lactose % m/m	Total solids % m/m
Original whey	0,28	0,98	3,31	4,48
UF permeate	0,21	0,25	3,00	3,46
UF retentate	1,63	9,32	4,61	15,56

The retentate was obtained from a reduction of the original volume by a factor 10. Flux values ranged between 20 and 10 $\ell m^{-2}h^{-1}$ which agrees well with the literature *(Breslau and Kilcullen, 1977* and *Fenton-May, 1971)*. The membrane used in the test was not of optimum type as can be seen from the results of the permeate analysis. About 72% of the proteins were retained, whereas the preferred figure is 95% or higher. The use of a membrane with lower molecular mass cut-off would remedy this situation. Protein and lactose content of the WPC compared favourably with that of whole milk and butterfat content with that of skim milk. The values compare well with those obtained by *Fenton-May (1971)*.

A retentate with a total solids content of 8% (volume reduction factor 5) would give a powder containing about 35% protein on a dry basis. Whey protein concentrate powders are typically classified into 35, 50 and 65% protein content.

7.3.2.2 Conclusions

The test results proved that WPC with a protein content equivalent to the norm could be obtained at flux rates similar to those reported for commercial membranes. With tailoring of the permeability and selectivity characteristics of the membrane, concentrates of different protein/lactose ratios could be obtained. The reclamation of proteins from whey, to maximise return on processing and to reduce disposal cost, by ultrafiltration compared with other processes, is discussed in detail by *Delaney (1974)*. The economics of the process were found to be favourable and as such a potential South African market for this type of application must exist. Creation and development of such a market will, however, with the present negative attitude of the dairy industry towards technology changes, require considerable time and effort.

7.3.3. EGG INDUSTRY

The use of UF in the egg industry is chiefly concerned with the concentration of both egg white and whole egg. After a successful pilot study using RO to reclaim proteins from waste water, the Egg Board showed considerable interest in the possible concentration of whole egg as well as protein reclamation from effluent by UF. Two bench studies were subsequently conducted; one for the production of concentrated whole egg (*i.e.* dewatering of fresh whole egg) and the other for reclamation of protein from effluent, for use as animal feed.

7.3.3.1 Concentration of whole egg

Fresh whole egg was concentrated from 24% to 41% solids at a feed pressure of 600 kPa and an average feed temperature of 29 °C.

Flux values and solids content of the concentrate and permeate during the concentration cycle are given in TABLE 7.5

TABLE 7.5 FLUX RATES AND SOLIDS CONTENT OF PERMEATE AND CONCENTRATE IN THE ULTRAFILTRATION OF WHOLE EGG

Volume recovery (%)	Solids content (%) Concentrate	Permeate	Flux rate ($\ell m^{-2}h^{-1}$)
0	23,68	1,15	6,3
25	30,67	1,10	6,7
50	41,29	1,35	3,5

Uijitenboogaart *(1982)* who compared various UF system configurations reports flux values ranging from 4,3 to 6,2 $\ell m^{-2}h^{-1}$ for similiar operating conditions and a dry-matter content in the permeate (loss of protein) of between 1,06 and 1,20%. The economics of the process were found to be about equal to those of the spray drying process. Since flux values similar to those reported in the literature were obtained during the bench study, it is felt that the UF technology could compete favourably against spray drying due to the lower capital cost associated with a local system compared to imported membrane technology.

7.4 EFFLUENT APPLICATIONS

7.4.1 PROTEINACEOUS EGG WASTES

Effluent from the Kraaifontein site (Cape Town) of the Egg Board posed a problem with regard to high volume and high COD loading, resulting in substantial charges being imposed on the factory by the local municipality for treating this type of effluent.

The effluent originates from the egg-breaking plant and contains valuable proteins and fats associated with whole egg. UF was envisaged for concentrating this effluent; the concentrate after spray drying could be used as animal feed, and for producing a permeate consisting mainly of water which could be used for floor-washing and direct disposal at greatly reduced COD levels.

Bench studies were performed to investigate membrane performance and operating parameters. The ability of the UF process to successfully concentrate the effluent for further processing and to produce permeate of acceptable quality was investigated initially. After positive results had been obtained from these first-order experiments, system operating conditions were scrutinised.

7.4.1.1 Type of effluent

Three major types of effluent could be distinguished, *viz* yellow, white and combined waste water. So-called yellow water contained mainly proteins from egg yolk, whereas white water consisted of albumen proteins. The combined effluent contained the yellow and white waters, usually in the ratio of about 2 : 98 parts by volume, respectively. The bulk of the effluent to be treated would be of the combined type, but its composition could be any combination of the yellow and white waters.

7.4.1.2. *Concentration of effluent*

Raw effluent was concentrated by batch mode with internal recycle to about 90% recovery by volume (volume reduction factor of 10). Initial and final solids content varied due to a variation in feed-stream composition. Average values are given in TABLE 7.6.

TABLE 7.6 SOLIDS CONTENT OF VARIOUS EGG EFFLUENTS AND UF PERMEATE AFTER CONCENTRATION BY A FACTOR OF 10

	Effluent Type		
	yellow	white	combined
% TS initial	2,3-2,5	0,8-0,9	1,3-1,4
% TS final	20,1-20,5	4,6-4,7	10,3-10,4
% TS permeate	0,60-0,90	0,15-0,20	0,20-0,65

COD values of the initial feed samples ranged from 5 000 to 15 000 mg ℓ^{-1}, while permeate showed typical values of 200 to 300 mg ℓ^{-1}. The activity of the enzyme lysozyme in the feed at levels of 2 500 to 14 000 units/mℓ was reduced to between 50 and 500 units/mℓ in the permeate. This enzyme was thought to inhibit the denitrification process at the downstream sewerage plant. At the time of writing this fact had not been proved, nevertheless endeavours were made to keep the lysozyme activity in the permeate as low as possible.

These values compare very favourably with those obtained by a chemical treatment process, especially with regard to the amount of proteins lost in the permeate. The cost of the UF process was also found to be competitive with the traditional chemical treatment process.

7.4.1.3 *Effect of feed temperature on flux*

Feed temperature was found to have a minor effect on the permeation rate. The relationship between feed temperature and flux was found to be linear and the effect became less pronounced as volume recovery increased. At zero recovery the slope of the curve was found to be 0,58 $\ell m^{-2}h^{-1}$ per degree temperature increase, while at 90% recovery the flux increase per degree temperature increase was 0,18 $\ell m^{-2}h^{-1}$. The effect is illustrated in FIGURE 7.17. The influence of a feed temperature increase on the flux rate thus changed from marginal at zero recovery to negligible at 90% recovery. Flux rate was thus considered to be insensitive to feed temperature for practical reasons.

7.4.1.4 *Effect of feed pressure on flux*

The average pressure was varied from 150 kPa to 650 kPa at zero recovery and at a constant feed temperature of 18 °C. In this range the variation in feed pressure had practically no influence on the permeation rate for the yellow and combined effluent. The effect is illustrated in FIGURE 7.18.

7.4.1.5 *Effect of velocity on flux*

Linear flow velocity was the only operating variable that had a substantial effect on membrane flux. An increase in the linear velocity resulted in an increase in flux, as expected. The relationship was found to be linear and slopes ranged from 0,9 $\ell m^{-2}h^{-1}$ for yellow water to 18,0 $\ell m^{-2}h^{-1}$ per velocity unit for combined effluent. The effect is illustrated in FIGURE 7.19. Unfortunately the practical operating velocity was limited to about 1,1 $m\ s^{-1}$ with the module configuration (two effluent type modules with series tube configuration coupled in series) envisaged for a commercial plant, due to pressure drop limitations.

7.4.1.6 *Operation mode*

Although an increase in recovery resulted in some decrease in flux, the permeation rate was found to be strongly time-dependent. Flux rate decreased exponentially with time and the rate of decline was virtually unaffected by the degree of recovery. Initial flux rate was halved in a matter of 5 to 6 hours. Flushing with cold water for 10 minutes resulted in complete restoration of original flux values, whereupon the decline was repeated. FIGURE 7.20 shows the concept of water flushing after 4 and 20 hours of operation. Rinsing with permeate proved unsuccessful and increased flux only marginally. Furthermore upon re-starting, the flux dropped almost immediately to the value that was maintained before flushing. Displacement of the effluent from the system with clean water and recirculation of small volumes of water also failed to restore flux values to their original levels. Recirculation of water with 70 ppm chlorine for 5 minutes however, restored flux values to the original.

The concentration cycle would thus entail a 22 hour per day production cycle with a 2 hour cleaning cycle consisting of several flushing actions every 4 to 6 hours of operation. Flushing could be effected by rinsing with fresh water or by circulation of a mild chlorine solution.

7.4.1.7 *Conclusions*

No reference to this type of application could be found in the literature. Nevertheless the author feels confident that commercially available membranes should not substantially out-perform the polyethersulfone membranes. Substantial revenue could therefore be collected from effluent treated by UF by selling the product as high protein animal feed after further processing.

FIGURE 7.17
Effect of temperature on flux : egg effluent

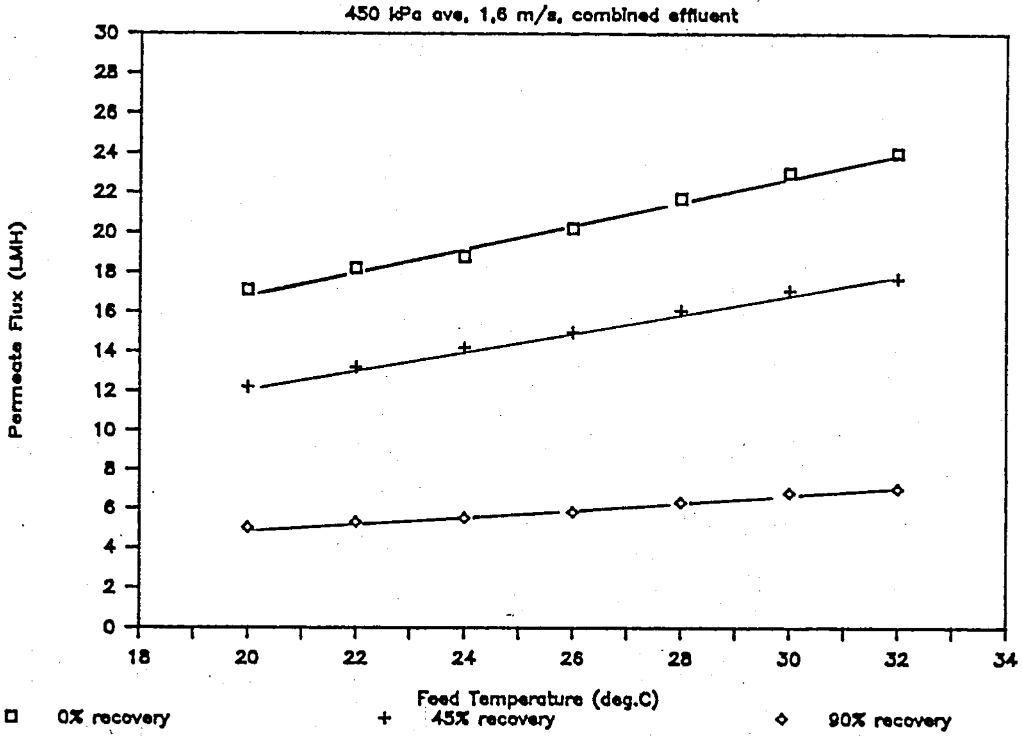


FIGURE 7.18
Effect of pressure on flux : egg effluent

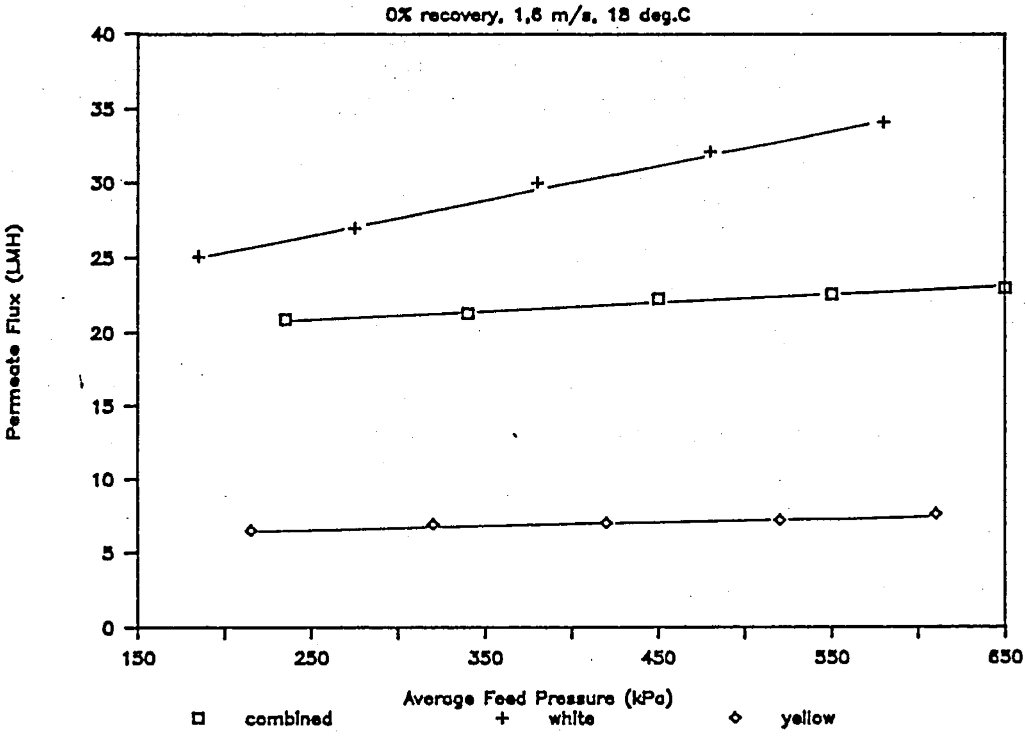


FIGURE 7.19

Effect of linear flow velocity on flux : egg effluent

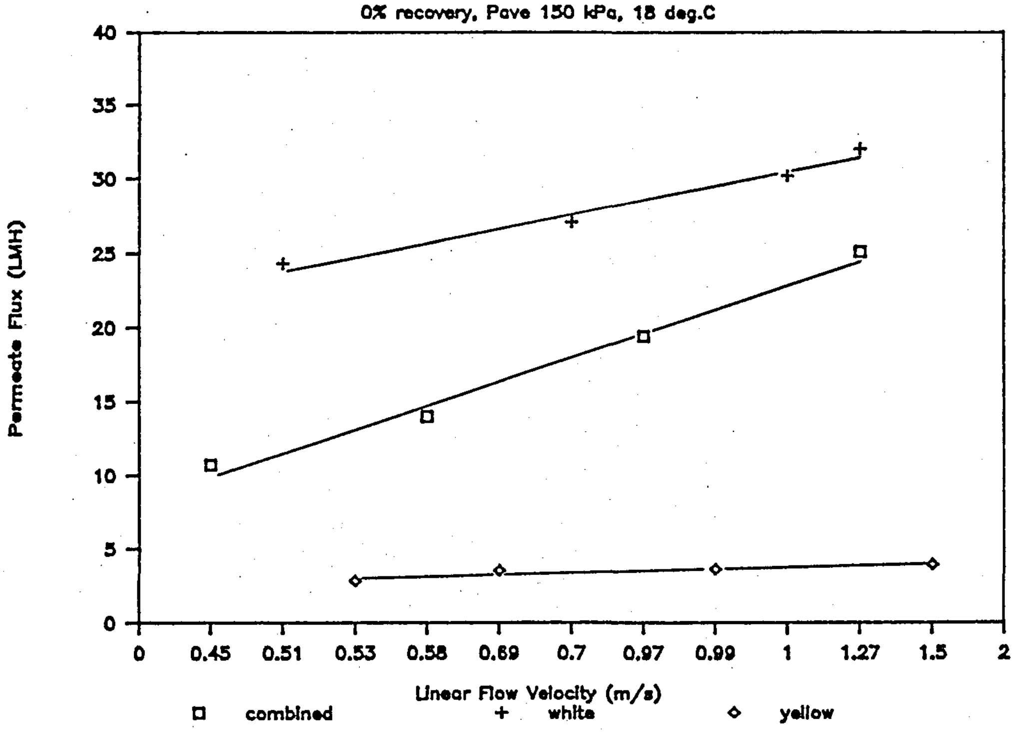
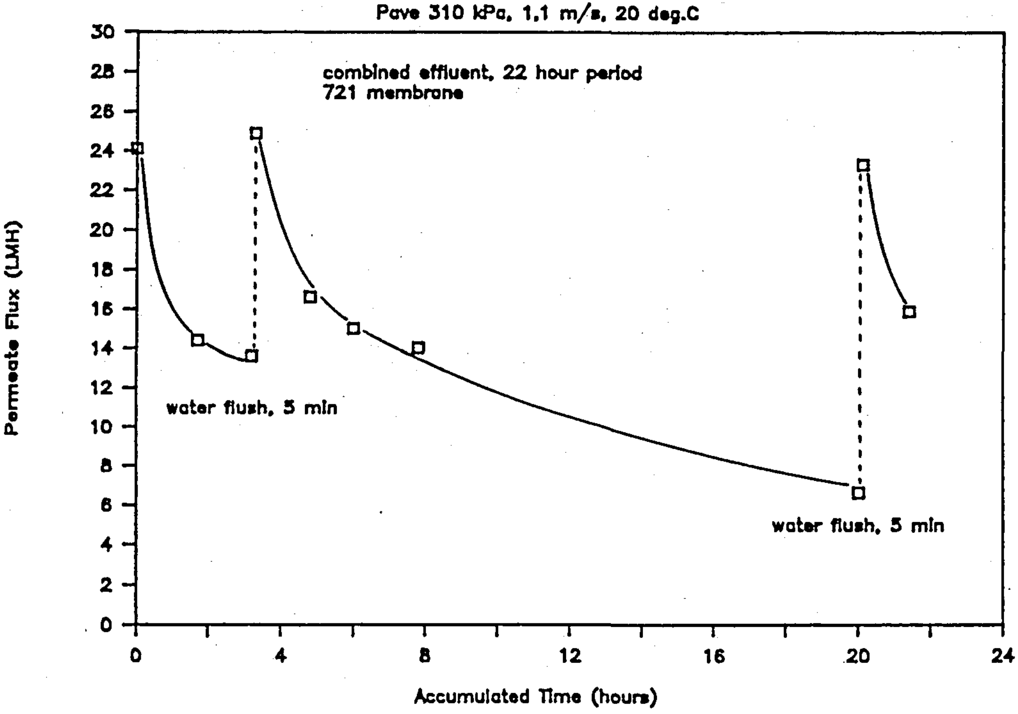


FIGURE 7.20

System operation mode : egg effluent



7.4.2 ANAEROBIC SLUDGE THICKENING

Industry today is faced with increased government action against the uncontrolled disposal of effluents from various sources. Local municipalities also have increased their charges for the treatment of effluent at local sewerage plants substantially.

Factors such as these created problems for a local wine producer in Stellenbosch. The particular producer was faced with an ultimatum imposed by the Department of Water Affairs. The effluent emanating from the wine distillery had to be treated to reduce the COD value to an acceptable level for disposal to the local sewerage plant, or the distillery would be forced to close down. To date the effluent has been disposed of on a dumping site since the cost of direct disposal to the sewerage plant would have been prohibitive. With a COD content of 40 000 mg ℓ^{-1} at a rate of 23 cents per kgCOD, the cost for the disposal would have been R9,20 per m^3.

The option of disposal of the effluent on a dumping site is being threatened by government action. Several means for reducing the COD content of the effluent were therefore investigated *e.g.* settling ponds, dissolved air flotation (DAF) and anaerobic digestion amongst others. Anaerobic digestion proved to be the most promising method, although several problems were associated with the process.

7.4.2.1 *Anaerobic digestion*

Anaerobic treatment of the organic distillery waste resulted in an effluent with a typical COD content of 10 000 mg ℓ^{-1}. Although this was a drastic reduction in COD content from the orginal of 40 000 mg ℓ^{-1}, this figure was still regarded as being too high for disposal to the local sewerage plant. Several problems arose with regard to process control and digester stability which affected the effectiveness of the process. The two major problems with the process described in detail by *Ross and Louw (1987)* were metabolic overloading and loss of biomass. Both ultimately resulted in the retardation or sometimes complete inhibition of the reaction. Reactivation was usually time-consuming due to the slow growth of anaerobic bacteria such as the methanogens.

It was therefore decided to investigate the use of ultrafiltration as a means for biomass retention on the anaerobic digester *(Ross et al., 1988)*.

7.4.2.2. *Ultrafiltration*

A single, effluent type (1,75 m^2 membrane area) ultrafiltration module, with membranes of 60 000 MMCO, was installed on-site during October 1987. The system consisted of a feed pump drawing activated sludge from the pilot reactor. The upflow anaerobic sludge blanket (UASB) digester of 2,4 m^3 operated at a mixed liquor suspended solids (MLSS) concentration of 30 kg m^{-3} and was fed with wine distillery waste at a rate of 3 kgCOD m^{-3} day^{-1} at 35°C. The sludge was then pumped through the UF module and the concentrate returned to the digester. Most of the permeate was routed to drain while a fraction was returned to the reactor since the permeate production rate exceeded the feed rate of raw effluent to the reactor by a factor of approximately eight. The module was operated under the following conditions:

feed pressure	400 kPa
outlet pressure	100 kPa
linear velocity	2 m s^{-1}
feed temperature	37 °C

A flow velocity of 2 m s^{-1} was chosen to curb excessive pressure losses and due to limitations on the feed pump, while simultaneously limiting membrane fouling through maintaining high shear rates. The pressure drop and velocity relationship is illustrated in FIGURE 7.21. A rapid increase in pressure drop occurred at velocities higher than 1,5 m s^{-1}, indicating that the maximum economical operating velocity would be limited to 2 to 2,5 m s^{-1}.

7.4.2.3. *Digestion process*

The process of anaerobic digestion was enhanced considerably by the use of ultrafiltration. Since biomass was retained almost completely, the concentration of bacteria in the reactor increased constantly to the point of zero growth. Anaerobic bacterial counts in the UF retentate and permeate were found to be 41 000 and 50 units per mℓ, respectively. During conventional operation, some biomass was always lost in the withdrawal of supernatant liquor from the reactor. The problem was compounded by foaming of the reactor contents. The use of anti-foaming agents had a detrimental effect on the growth rate of the anaerobic bacteria.

The practically complete retention of biomass enabled the reactor to operate at higher organic loadings since the biomass concentration could be increased *(Anderson et al., 1986)*. Traditional space-load rates of 2 to 3 kgCOD m^{-3} day^{-1} could be increased to 7 to 8 kgCOD m^{-3} day^{-1}. This in effect meant lowering the retention time to a third of the usual or, alternatively, reducing the reactor size by a factor of three. Gas (methane) production increased by a factor of between 2 and 3 when compared with the conventional anaerobic process.

According to *Ross and Louw (1987)* gas production and COD loading rate are the two major indicators of reactor performance and it is obvious that the use of UF resulted in a substantial increase of reactor efficiency.

7.4.2.4 *Permeate quality*

UF permeate, alternatively final effluent, was of sufficient good quality for disposal to drain, *i.e.* local sewerage plant. The permeate had a typical COD value of 500 mg ℓ^{-1} and a suspended solids concentration of 6 to 8%. COD reduction based on feed to the module (sludge from the digester had a typical COD content of 10 000 mg ℓ^{-1}) ranged from 80 to 95%.

7.4.2.5 *Flux values*

Since the mesophilic digestion process dictated an operating temperature of 37 °C, temperature effects on flux were not investigated. However, flux rates were found to increase with increases in feed pressure and linear velocity. The effects are illustrated in FIGURE 7.22. Although the module was subjected to an infrequent cleaning procedure (approximately once per month), flux values remained relatively stable throughout the 4 000 hour test period. It was realised at a later stage that the decline in flux (illustrated in FIGURE 7.23) was due to an increase in the solids concentration of the feed stream and membrane fouling by biomass. Flux values could be restored by washing the membranes with a chlorine solution. Extreme care was taken to remove all traces of washing solution from the system so as not to contaminate reactor content.

7.4.2.6 *Advantages of UF*

There are several advantages in the use of UF in biological waste treatment systems such as anaerobic digestion. These advantages are a direct result of the greater biomass retention which can be effected by UF:

i) The need for a settling unit is eliminated, *i.e.* the reactor can be a mixed reactor. No biomass separation problems are experienced during system overloads.
ii) Higher biomass concentrations can be achieved, minimising reactor volume, thus capital and operating costs.
iii) The final effluent is of superior quality.

7.4.2.7 *Conclusions*

The experiment showed that the use of UF in conjunction with anaerobic digestion could solve organic effluent problems. In addition to providing a solution to the effluent problem, the use of UF improved the efficiency of the anaerobic digestion process at economical flux levels.

FIGURE 7.21
System pressure drop *vs.* velocity : distillery effluent

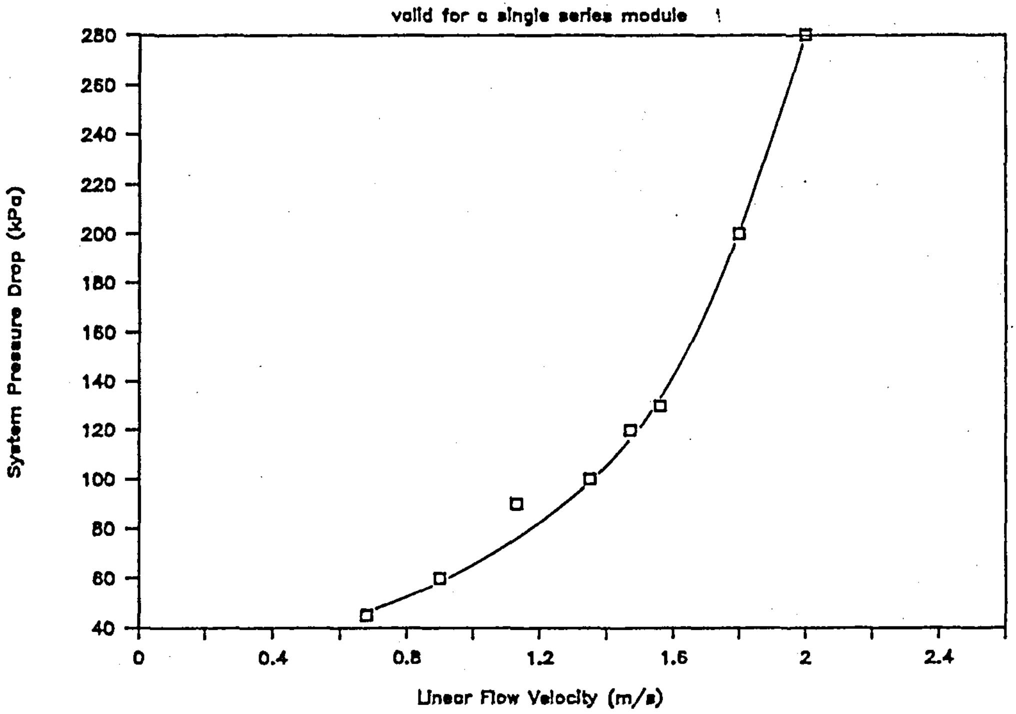


FIGURE 7.22
Flux *vs.* pressure at various velocities : distillery effluent

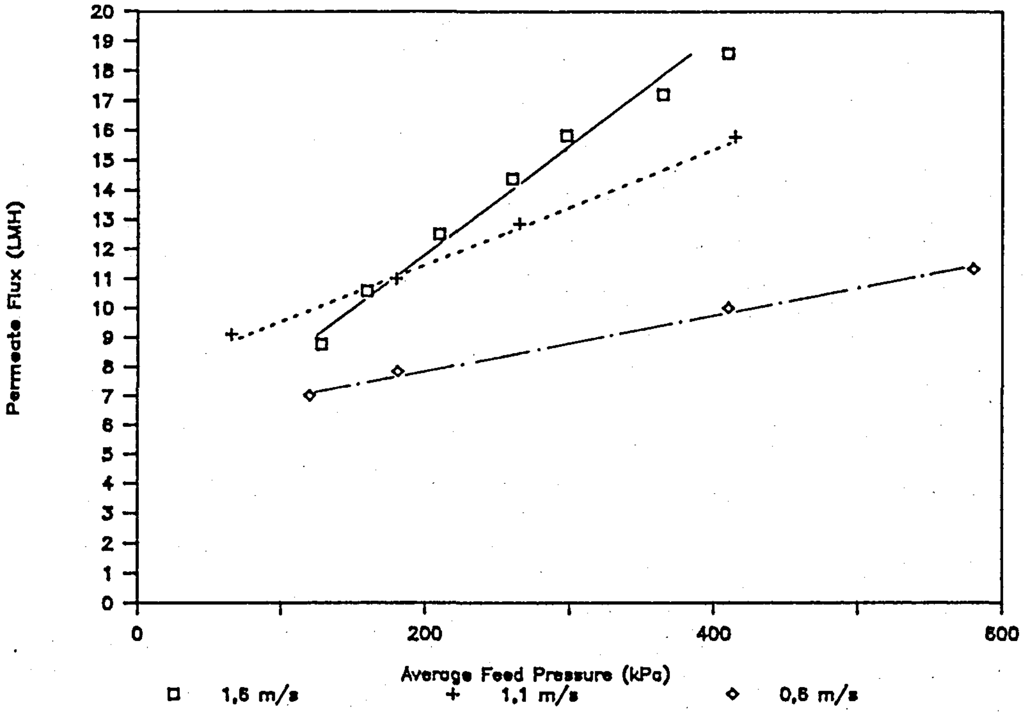
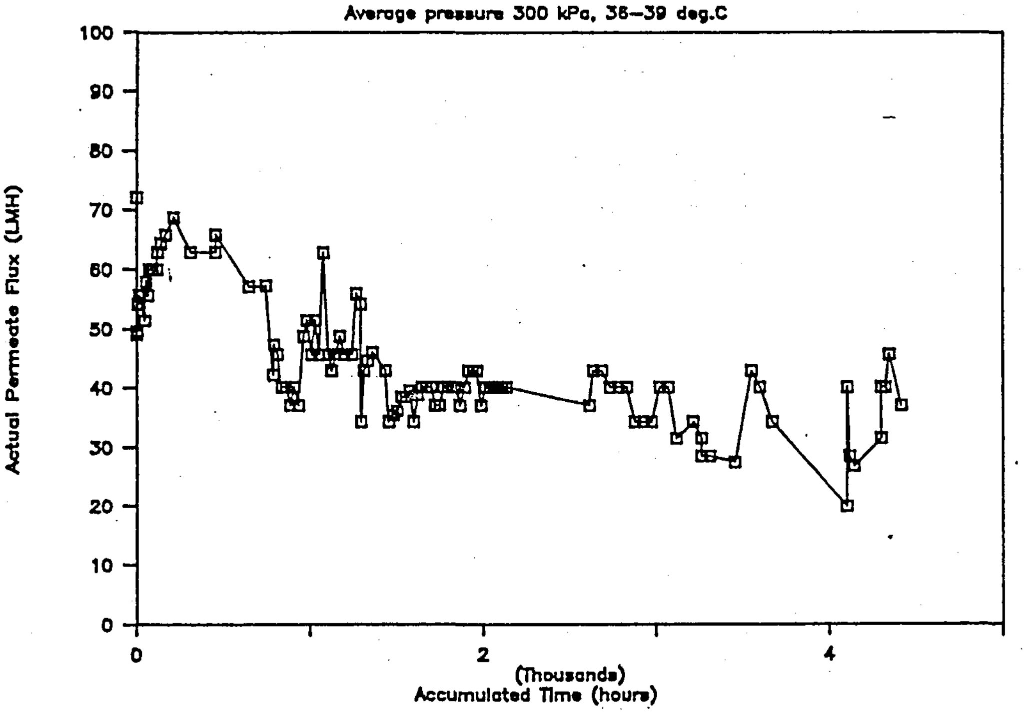


FIGURE 7.23
Flux *vs.* time : distillery effluent



7.4.3 TREATMENT OF SASOL EFFLUENT

The investigation into application of reverse osmosis for the upgrading of various Sasol effluent streams was done by Sastech during 1987.

During these trials the following streams were investigated with BINTECH (Membratek) tubular reverse osmosis equipment, using cellulose acetate (CA) membranes:

i) stripped gas liquor;
ii) bio-effluent;
iii) dual media filtration effluent (DMFE).

Because of the promising data that were obtained during these investigations, it was decided to test BINTECH reverse osmosis membranes on DMFE at pilot plant level, to determine the application of RO as a process for effluent treatment.

It is known that the performance of the RO process is strongly dependent on the quality of pre-treatment and it was suggested that the possible use of local UF technology for pre-treatment for RO should be investigated. As a result a single UF module was installed on site at Secunda for test work on DMFE which commenced in August 1987.

Although the UF test was done on a small scale, extensive studies were carried out, which resulted in the collection of substantial data under actual process conditions.

7.4.3.1 *On-site testing conditions and equipment*

On-site testing of the UF process started on 21/8/87. Utility water acting as feed to the module was obtained from Unit 52 (feed from 52PC-106). The UF membrane used, had an approximate molecular mass cut-off of 40 000. The module was driven by using available process line pressure (300 kPa).

7.4.3.2 *Study objectives*

The main objectives during this study were as follows:

i) to obtain quantitative data on UF permeate quality;
ii) to establish first order flux values;
iii) to determine flux stability;
iv) to make a preliminary selection of cleaning chemicals.

7.4.3.3 Operating conditions

The following operating variables were logged during the test:

feed temperature
permeate flow
concentrate flow
permeate conductivity
concentrate conductivity
inlet pressure
outlet pressure

Daily analysis comprised the following:

concentrate COD
permeate COD
concentrate turbidity
permeate turbidity
feed suspended solids concentration

Water recovery was maintained at 9 - 10%, inlet pressure at 300 kPa in and outlet pressure at 100 kPa, temperature varied between 10 and 40 °C and linear flow velocity ranged from 1,4 to 1,6 m s^{-1}.

Caustic, soap and chlorine washes were applied to restore flux values.

7.4.3.4 Summary of results

7.4.3.4.1 *Filtrate quality*

Permeate COD values ranged from 160 to 320 mg ℓ^{-1} corresponding to a reduction of COD content of 48 to 62% (based on concentrate COD). Turbidity of permeate varied from 4 to 10 NTU and reduction from 76 to 93% (based on turbidity of concentrate). Turbidity values could be affected by the brown colour of the permeate, since the values would seem rather high. Ultrafiltration normally yields turbidity values of less than 1 NTU. TDS of the permeate was reduced by roughly 50 to 90% which resulted in permeate TDS values of 400 to 800 mg ℓ^{-1} (mean value about 600 mg ℓ^{-1}). Average plugging index at 5 minutes was 87,9% with a high of 95,2% and a low of 77,0%. The average value of the plugging index at 10 minutes was calculated as 92,3% with a high of 96,9% and a low of 86,0%.

7.4.3.4.2 *Flux values and stability*

Flux values varied greatly due to feed temperature variation and degree of fouling (refer FIGURE 7.24). Mean flux values were maintained at about 40 $\ell m^{-2}h^{-1}$ throughout the 2 000 hours of the study by regular washing, with high and low values at approximately 95 and 15 $\ell m^{-2}h^{-1}$, respectively.

7.4.3.4.3 *Membrane fouling and cleaning chemicals*

Due to the nature of DMFE, the membranes were fouled relatively quickly, resulting in severe flux decline. Flux values could be restored by washing with detergent and/or chlorine solution. The frequency of the washing cycles ranged between 24 and 160 hours of operation, depending on feed water quality and mode of operation.

7.4.3.5 Discussion

During the study it was evident that the fouling rate, feed water composition, feed water temperature and flux rate were all interdependent.

Since it was impossible to control the feed temperature (process line was not insulated and exposed to environment), and because virtually no other variables could be maintained at a constant level the investigation of the effect of individual operating variables on flux could not be determined.

Operating variables could therefore not be optimised to suit the particular application. Nevertheless the results obtained, showed that long-term flux stability was possible with the adopted cleaning procedure. Again it must be stressed that the method of washing used during the test was not necessarily optimum with respect to operating cost (concentration, temperature and time), but merely served to restore membrane flux to its original value.

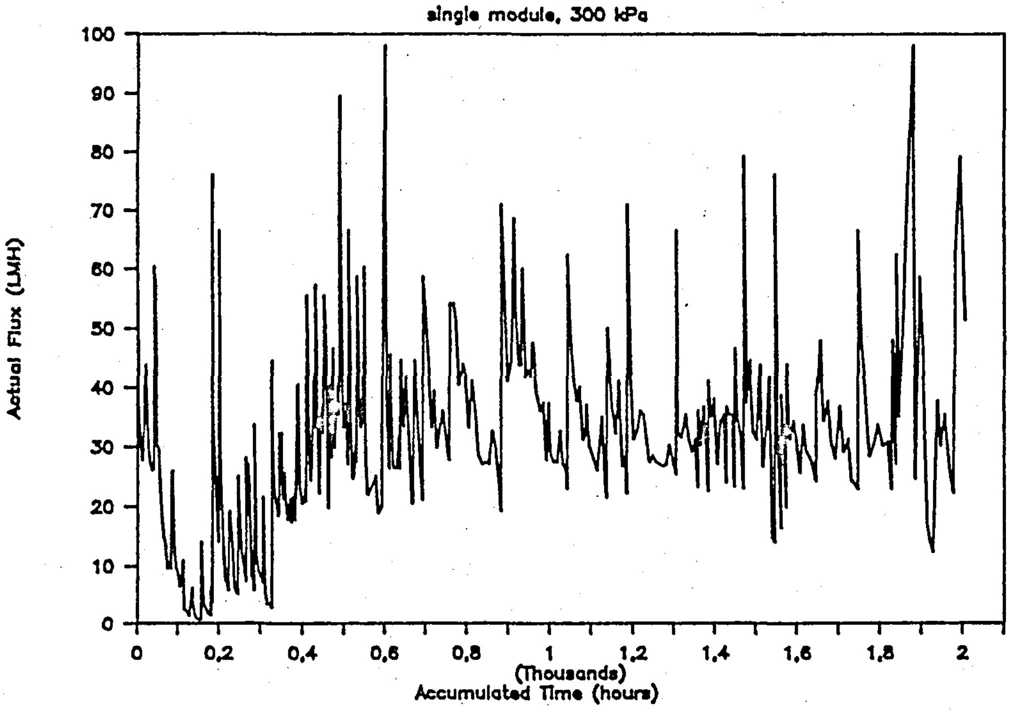
The test further proved that UF could provide filtrate of acceptable quality. Again the membrane used in the test was selected at random and was not necessarily the ideal type in terms of cut-off for this application.

7.4.3.6 Conclusions

The test showed that UF could solve the effluent treatment problems on some of the process streams at Sasol. Furthermore, stable flux values could be maintained under the correct operating conditions.

Flux values could be improved substantially by optimising membrane cut-off and operating conditions for the particular application. This would drastically favour the economics of the process.

FIGURE 7.24
Flux *vs.* time : Sasol DMFE



7.4.4 CONCENTRATION OF OIL/WATER EMULSIONS

Metal machining operations use a relatively dilute mixture (2 to 5%) of oil in water as a cutting lubricant and coolant. As this mixture is degraded in normal operations, wastes are generated which require disposal. The oil always presents a disposal problem, even if it is not classified as hazardous, because it is difficult to process in conventional sewerage treatment systems. Ultrafiltration (UF) membranes can be used to recover the water from this oil/water waste mixture and to concentrate the oil to a very high degree, resulting in a significant reduction in the waste volume sent for disposal.

Removal and recycling of the water from the oil waste emulsion will serve several desirable purposes. First, if disposed of as hazardous waste, the concentrate will be reduced in volume by about a factor of ten and will be of sufficient organic concentration to support combustion if incineration is required or desired. Second, in a concentrated form, the oil may be amenable to cleanup procedures and subsequent reuse in machining operations. Third, the clean water produced can be reused to dilute fresh or recycled oil, or used as a makeup to replace water evaporated from the recirculating oil in the course of normal operations. The recovered water in any case is usually of sufficient purity for disposal in conventional sewerage treatment plants.

The use of ultrafiltration for the separation/concentration of oil/water emulsions has become more frequent since the development of hydrophilic, synthetic UF membranes. Membranes made from hydrophobic materials, such as polysulfone, typically show poor fluxes in this type of application.

The motivation for this bench study was to see whether membranes made from polyethethersulfone could show performance similar to that of polyamide or polyacrylonitrile membranes for this particular application.

Oil/water emulsions were prepared by the addition of fresh cutting oil to tap water at a starting concentration of 2 g ℓ^{-1}. This is a typical concentration used in the industry for cutting and cooling operations.

The emulsion was then concentrated by operating a UF system in a batch mode with internal recycle. Emulsion was fed from a batch tank through the UF system by means of a feed pump and again returned to the tank, while permeate was drawn off continuously.

7.4.4.1 *Flux values during concentration*

A starting oil concentration of 2 g ℓ^{-1} was used and concentrated to 20 g ℓ^{-1} by removing 90% of the original volume as permeate. A final oil concentration of 50% or 500 g ℓ^{-1} as mentioned in the literature *(Berghof, 1985)* translates to a 99,6% recovery by volume or 0,4% of the original volume being retained as concentrate. This could not be achieved during the bench test since this would require very large sample volumes. Instead, higher recoveries, or oil concentrations in the concentrate, were simulated by the addition of oil to the batch tank.

The decline in flux from 48 to 12 $\ell m^{-2}h^{-1}$ was experienced during the concentration. A gradual decline was experienced initially, following an almost linear relationship. At about 95% recovery, corresponding to a feed concentration of 40 g ℓ^{-1}, a sharp decline occurred due to the rapid increase in oil content in the feed stream.

Nevertheless, the flux values compared favourably with those cited in the literature for hydrophilic membrane types.

7.4.4.2 *Effect of feed pressure on flux*

Feed pressure was found to have a negilgible effect on the flux rate, especially at higher feed concentrations. The effect is illustrated in FIGURE 7.25.

An increase in feed concentration results in decreased flux which is practically pressure-independent at feed concentrations above 40 g ℓ^{-1}.

7.4.4.3 *Effect of feed concentration on flux*

It follows from FIGURE 7.25 that the flux declined linearly with an increase in feed concentration at higher oil concentrations. The decline, at a feed temperature of 22 °C, was approximately 0,13 $\ell m^{-2} h^{-1}$ per 1 g ℓ^{-1} concentration increase.

7.4.4.4 *Flux stability*

Flux values remained relatively stable over prolonged periods. A 22% decline was noted over a 67 hour period with a feed stream having an oil concentration of 210 g ℓ^{-1}. This is equivalent to a decline rate of about 0,043 $\ell m^{-2} h^{-1}$ per hour. Long-term studies will be required to determine whether the decline rate levels out.

7.4.4.5 *Permeate quality*

Permeate appeared clear and samples were analysed for COD in order to obtain an indication of the oil concentration. These values were compared with the COD of standard oil solutions. The results are tabulated below:

Sample	COD (mg ℓ^{-1})
tap water	15
permeate	70 - 100
0,25 g ℓ^{-1} oil in tap water	705
1,0 g ℓ^{-1} oil in tap water	1350
10 g ℓ^{-1} oil in tap water	3465

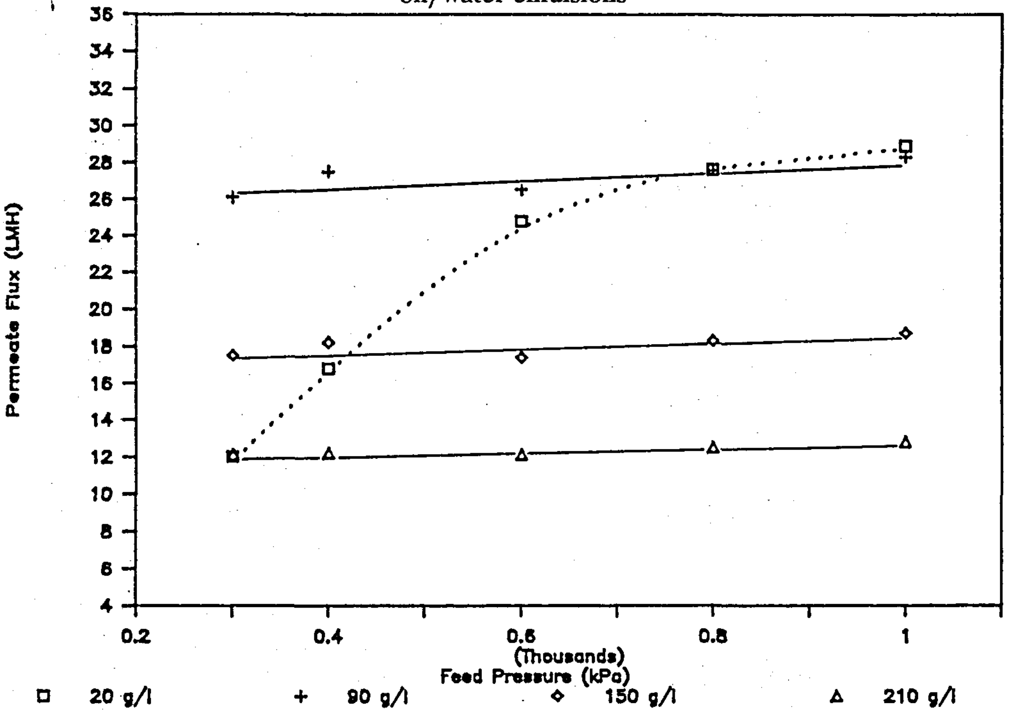
As such it would seem that the permeate contained not more than about 30 mg ℓ^{-1} of oil.

7.4.4.6 *Membrane cleaning*

The short study indicated that membrane fouling was not severe and that cleaning could be effected by flushing with clean water.

FIGURE 7.25

Effect of pressure and feed concentration on flux
oil/water emulsions



7.4.5 TANNERY EFFLUENT

The possible use of UF in the tanning industry is described in the literature by *Drioli (1980)* as well as *Drioli and Cortese (1980)*. They found that the tanning industry,in Italy and Europe partiularly, is faced with the problem of controlling and reducing the pollution in their effluents especially because of recent stricter laws directed towards this problem.

The problem experienced by a local tannery was the amount and cost of chemicals used in their chemical treatment step of their effluent plant and the large volume of sludge which subsequently had to be dried in open drying pans. The drying of the sludge posed a problem, especially in the rainy winter season, when these pans were flooded, resulting in contamination of nearby natural water scources.

Screened, raw effluent (fat removed) was subjected to UF without additional chemical treatment, except the addition of $Al_2(SO_4)_3$ at 500 ppm concentration level. This resulted in a lowering of the original pH of 13,5 to a more acceptable value of 7,0 and served to bring about excellent floc formation, aiding the UF process.

Flux values decreased linearly from 230 $\ell m^{-2}h^{-1}$ to 50 $\ell m^{-2}h^{-1}$ through the 0 to 95% volume recovery range at a feed pressure of 400 kPa and a feed temperature of 14 °C.

Permeate was clear at all times and contained all the chemicals (Na_2S/NaSH) used in the dehairing process. As such the permeate could be returned to the dehairing treatment baths. The concentrated sludge was of sufficient low water content for drying or possible incineration.

These results showed that UF could, with a minimum of pretreatment, concentrate raw tannery effluent for disposal to give a more concentrated sludge, eliminate most chemicals used in the conventional settling process and possibly reclaim dehairing bath ingredients.

CHAPTER EIGHT

COMMERCIAL PLANTS

8.1 INTRODUCTION

As a result of the various successful bench and pilot studies outlined in the previous chapter, several contracts were awarded for the supply of small and medium-sized ultrafiltration plants.

Production plants in both the food and effluent treatment application fields were supplied. Two small plants of 25 and 50 m^3day^{-1} capacity were supplied to the food industry for the reclamation of fruit juice from sludge following the normal clarification process *(Strohwald, 1987)*. These plants are envisaged as pioneering steps in paving the way for the possible sale of two full-scale (350 m^3day^{-1}) juice clarification plants towards the 1990 season. A larger plant of 120 m^3day^{-1} capacity was requested by the Egg Board for the reclamation and concentration of proteins from egg waste waters. This plant is scheduled for commissioning during July/August 1988.

8.2 FOOD APPLICATION

Two small ultrafiltration plants were supplied to fruit processors at Ceres for the clarification of fruit juice and reclamation of juice from sludge.

8.2.1 CERES FOOD INDUSTRIES (CFI)

A 25 m^3day^{-1} plant for the clarification of fruit juice and sludge was installed at Ceres Food Industries, Ceres, at a capital cost of R61 000 towards the end of 1987. The plant consists of one series train of 20 modules with parallel tube configuration providing a total membrane area of 40 m^2, with possible expansion to 30 modules (60 m^2). Flux data obtained during a typical production run treating quava sludge is shown in FIGURE 8.1. The plant performed well above the design flux figures and customer feed-back was very positive.

8.2.2 CERES FRUIT GROWERS (CFG)

A 50 m^3day^{-1} ultrafiltration plant for sludge clarification was commissioned at Ceres Fruit Growers, Ceres, during November 1987. The plant consists of 2 parallel trains of 15 modules each (*i.e.* 30 in total), expandable to 20 modules per train. Total membrane area at present is 60 m^2, but can be increased to 80 m^2 with the additional modules. Capital cost for the plant was R105 000 which included an optional membrane guarantee.

It was found that operating costs for sludge treatment were considerably reduced through the use of ultrafiltration and that the disposal of waste sludge was made easier since the final concentrated sludge volume could be reduced considerably.

A cost comparison between UF and traditional sludge treatment is given below and summarised in TABLE 8.1

Operating cost for the UF process was found to be about 54% of the traditional filter process. Extra juice yields of 10 - 20% could be obtained with the use of UF, but this was not brought into account. The pay-back period for the UF plant was calculated at about 7 months.

COST COMPARISON : SLUDGE TREATMENT

Ultrafiltration plant

Basis:	capacity	50 $m^3 day^{-1}$
	recovery	75%
	depreciation	5 years, straight line
	operating time	22 hours per day
	capital cost	R 92 000

Power cost

feed pump	18	kW	
specific comsumption	0,36	kWh/m^3	
cost @ 7c/kWh	2,52	c/m^3	→

Cleaning chemicals

0,3 kg NaOH @ 800 c/kg	240	c	
0,2 kg HTH @ 500 c/kg	100	c	
3 m^3 water @ 60 c/m^3	180	c	
total	520	c	
specific cost	10,40	c/m^3	→

Membrane replacement

production hours per year	3500		
approximate lifetime	7000	hours	
total capacity per lifetime	381 500	m^3	
cost of 30 replacement sets	12 000	R	
specific cost	3,15	c/m^3	→

Manpower

manual control period	8	h/day	
labour rate	10	R/h	
specific cost	160	c/m^3	→

Investment

capacity per year	190 750	m^3	
interest @ 20%	9,65	c/m^3	
depreciation (5 years)	9,65	c/m^3	
total	19,30	c/m^3	→

Traditional filter

Basis:	capital cost filter press	R	40 000
	capital cost Schenk filter	R	178 000
	total	R	218 000

Power cost

filter press	8	kW	
Schenk filter	22	kW	
specific comsumption	0,60	kWh/m^3	
cost @ 7 c/kWh	4,20	c/m^3	→

Chemical cost

0,56 kg/m^3 kieselghur @ 135 c/kg	75,6	c/m^3	
0,20 kg/m^3 bentonite @ 78 c/kg	15,6	c/m^3	
total specific cost	91,20	c/m^3	→

Manpower

manual input time	14	h/day	
rate	8	R/h	
specific cost	224	c/m^3	→

Investment

capacity per year	190 750	m^3	
interest @ 20%	22,88	c/m^3	
depreciation (5 years)	22,88	c/m^3	
total	45,76	c/m^3	→

TABLE 8.1 OPERATING COST COMPARISON FOR SLUDGE TREATMENT

	UF (c/m^3)	TRADITIONAL (c/m^3)
Chemicals	10,40	91,20
Membranes	3,15	0
Power Consumption	2,52	4,20
Manpower	160,00	224,00
Running Costs	176,07	319,40
Investment	19,30	45,74
TOTAL	195,37	365,14

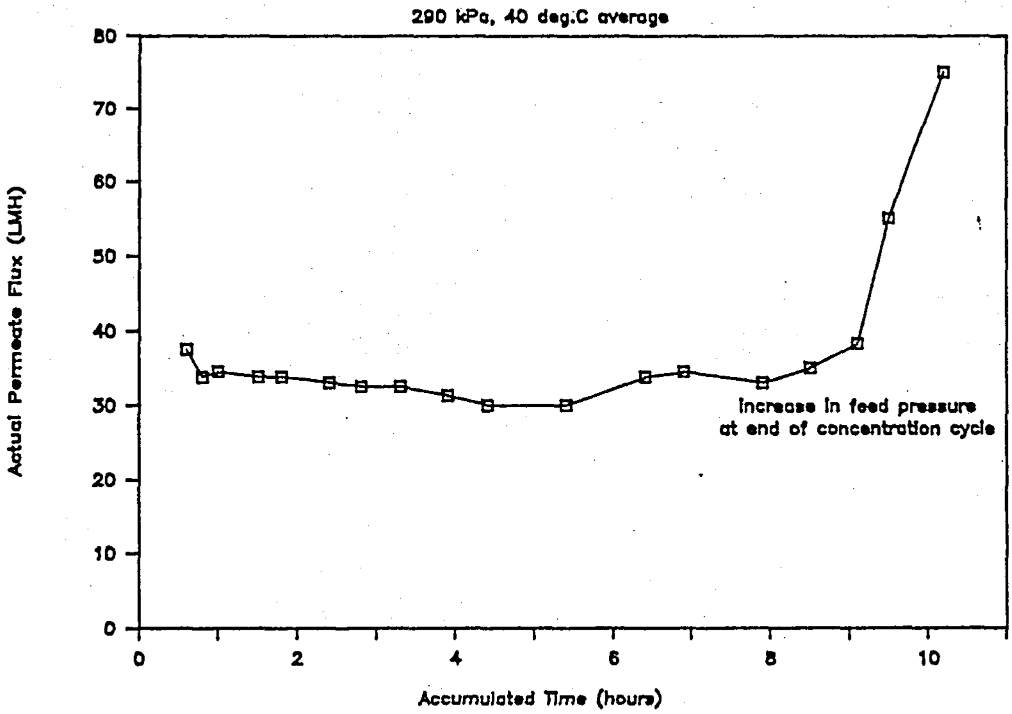
8.3 EFFLUENT APPLICATION

A contract was awarded to Bintech by the Egg Board during February 1988 for the supply of a 120 m^3day^{-1} UF plant. Contract price was R276 000. The plant was designed to reclaim and concentrate proteinaceous egg waste from wash water. The liquid protein concentrate was to be spray dried at another site and utilised as livestock feed (poultry and pets).

The plant consists of 200 effluent type modules with series tube configuration resulting in a total membrane area of 350 m^2. The scope of supply included the complete ultrafiltration system as well as certain civil works *eg.* 10 m^3 permeate tank and 90 m^3 feed buffer tank.

FIGURE 8.1

UF plant performance : guava sludge



CHAPTER NINE

CONCLUSIONS

The objectives of this thesis were pointed out in CHAPTER ONE and the purpose of this final chapter is to evaluate whether these objectives have been met in a satisfactory manner. The objectives were fourfold and are given below:

i) to establish the technology required for the production of commercially useful tubular ultrafiltration membranes made from polyethersulphone;
ii) to incorporate these membranes into modules for use in the industry;
(iii) to evaluate these membranes and modules in the industry through bench/pilot studies;
(iv) to commercialise the technology through the construction of industrial-sized UF plants.

9.1 ESTABLISHMENT OF MEMBRANE TECHNOLOGY

With regard to the first objective it can be argued that the membranes which were developed, showed good integrity and quality when compared to commercial membranes (refer to CHAPTER FIVE section 5.5). The materials selected for membrane manufacture were current state-of-the-art materials and are discussed in CHAPTER THREE. Although the selection and use of such materials do not warrant good membrane integrity and quality, it is felt that commercially useful, although perhaps not optimum, tubular ultrafiltration membranes have been developed. This fact is substantiated by the positive results obtained from bench and pilot studies with actual process streams which are described in CHAPTER SEVEN. Membrane performance and product quality in the applications which were investigated, compared well with results reported in the literature for commercial systems, despite the fact that no effort was made to develop membranes with optimum performance for each application.

9.2 DEVELOPMENT OF TUBULAR ULTRAFILTRATION MODULES

The second objective of ultrafiltration module development was realised through the modification of existing tubular RO module technology which is described in CHAPTER SIX. The achievement of this objective is illustrated by the successful operation of such modules in industrial UF plants (section 8.2).

9.3 EVALUATION OF ULTRAFILTRATION TECHNOLOGY

The developed UF technology was evaluated through bench/pilot studies which are described in CHAPTER SEVEN. Real process streams were used in these studies to obtain information about the performance of membranes and modules in an industrial environment. Ultrafiltration showed potential in the fruit juice processing industry (section 7.3.1) especially in the clarification of fruit juice sludges where improved end-product quality (section 7.3.1.2) and economics (section 8.2.2) were realised. UF also showed promise as a separation process in the reclamation of egg proteins from waste water (section 7.4.1), so much so that a sale for the construction of a 120 m^3 per day plant was realised (section 8.3).

9.4 COMMERCIALISATION OF ULTRAFILTRATION SYSTEM

The objective of technology industrialisation was met through the investigation of various applications (CHAPTER SEVEN) of which two in particular resulted in the construction of commercial plants (refer to CHAPTER EIGHT sections 8.2 and 8.3). To date these plants have performed well in terms of membrane and module integrity. The development of the product can thus be seen as having completed the full cycle from basic membrane and module development, through pilot studies, to commercial plant status.

BIBLIOGRAPHY

Anderson, G.K.; Saw, C.B. and Fernandes, M.I.A.P. (1986). "Applications of porous membranes for biomass retention in biological wastewater treatment processes"; Process Biochemistry, December, *174.*

Applegate, L.E. (1984). "Membrane Separation Processes"; Chemical Engineering, June 11, *64.*

Bakke (1980). "Liquid flow device"; SA patent, SA 80/7213.

Ballintyn, N.J. (1982). In "Kirk-Othmer Encyclopedia of Technology"; 3rd ed. Wiley, N.Y. volume 18, *833.*

Blatt, W.F. (1976). "Principles and practice of ultrafiltration" in Membrane Separation Processes, Ed. P. Meares, Elsevier, Amsterdam.

Barton, A.F.M. (1983). "Handbook of solubility parameters and other cohesion parameters"; CRC Press, Boca Raton, Florida U.S.A., *59.*

Beaton, N. (1977). "Applications and economics of ultrafiltration", International Chemical Engineering Symposium Series 51, *59.*

Bechhold, H. (1907). Kolloidal Zeitung 1, *107.*

Bechhold, H. (1908). Biochemie Zeitung 6, *379.*

Berghof (1985). "Ultrafiltration von Oel-Wasser Emulsionen"; Technical Bulletin 2/85.

Bottino, A.; Capannelli, G.; Munari, S. and Turturro, A. (1988). "High performance ultrafiltration membranes cast from LiCℓ doped solutions"; Desalination 68, *167.*

Breslau, B.R. and Kilcullen, B.M. (1977). "Hollow fiber ultrafiltration of cottage cheese whey : performance study"; Journal of Dairy Science 60, *1379.*

Breslau, B.R.; Milnes, B.A.; Short, J.L. and Tump, J. (1984). "The application of ultrafiltration to fruit juice processing"; Romicon report, February 1984.

Cabasso, I. (1977). Appl. Polym. Sci. 20, *2377.*

Cabasso, I. (1980). "Practical aspects in the development of a polymer matrix for ultrafiltration" in Ultrafiltration Membranes and Applications; Ed. A.R. Cooper, Plenum, N.Y.

Cadotte, J.E. (1976). Report OWRT/S76 401 U.S. Department of the Interior, Washington, DC.

Capannelli, G.; Vigo, F. and Munari, S. (1983). "Ultrafiltration membranes - characterisation methods"; Journal of Membrane Science 15, *289.*

Cartwright, P.S. (1982). in "Proceedings of the 10th Annual WSIA Conference"; volume 2, session 6, July.

Cherkasov, A.N.; Polotskii, A.E.; Gorelova, L.; Zhemkov, V.P. and Belen'kii B.G. (1981). "Use of gel chromatography to characterise UF membranes"; English translation from Kolloidnyi Zhurnal 43, no 4, *804.*

Cheryan, M. (1986). in "Ultrafiltration Handbook"; Technomic Publishing Company, Lancaster, Pennsylvania, U.S.A.

Cooper, A.R. (1982). "Membrane testing using polymeric dyes"; Separation Science and Technology 17(4), *621.*

Deanin, R.D. (1972). in "Polymer Structure, Properties and Applications"; Chaners Books, Boston, MA.

Delaney, R.A.M.; Donnelly J.K. and Bender, L.D. (1974). "Whey processing by ultrafiltration part 1"; Dairy Industries, Nov.74, *426.*

Doesburg, J.J. (1965). "Pectic substances in fresh and preserved fruits and vegetables"; Inst. for Research on Storage and Processing of Horticultural Produce, Wageningen, The Netherlands, *19* and *119.*

Downes, T.E.H. (1987). (Animal and Dairy Science Research Institute, Irene, RSA) Personal communication.

Dreger, D.R. (1978). Mach. Des. 50(1), *114.*

Drioli, E. (1980). "Progress in the industrial realisations of ultrafiltration processes" in Ultrafiltration Membranes and Applications; Ed. A.R. Cooper, Plenum, NY, *291*.

Drioli, E. and Bellucci, F. (1978). Desalination 26, *17*.

Drioli, E. and Cortese, B. (1980). "Ultrafiltration processes for pollution control and chemical re-use in the tanning industry"; Desalination 51, *131*.

Drzewinski, M. (1985). Journal of Applied Polymer Science 30, *4753*.

Dutka, B.J. (1981). "Membrane Filtration : Applications, Techniques and Problems"; Marcel Dekker, NY.

Elford, W. (1930). Proc. R. Soc. B106, *216*.

Fane, A.G.; Fell, C.J.D. and Waters, A.G. (1981). Journal of Membrane Science 9, *245*.

Fenton-May, R.I. (1971). "Use of UF/RO systems for the concentration and fractionation of whey"; Journal of Food Science 36, *14*.

Gekas, V. (1988). Desalination 68, *77*.

Gekas, V.; Hallstrom, B. and Tragardh, G. (1985). "Food and dairy applications : the state of the art"; Desalination 53, *95*.

Glover, F.A. (1985). In "Ultrafiltration and reverse osmosis for the dairy industry"; National Institute for Research in Dairying, Reading, England.

Goldsmith, R.L. (1975). J. Eng. Ind. 97, *238*.

Hanemaaijer, J.H. (1985). Voedingsmiddelen-technologie 18, *26*.

Hansen, C.M. (1970). Journal of Paint Technology 42, *660*.

Hansen, R. (1977). "Feta cheese production by UF"; Nordeuropaeisk Mejeri-Tidskrift, *9*.

Heatherbell, D.A. (1977). "Apple juice clarification by UF"; Confructa, 22(5/6), *157*.

Hedrick, T.I. (1983). "Reverse Osmosis and Ultrafiltration in the Food Industry : Review"; Drying Technology 2(3), *329*.

Iwama, A. and Kazuse, Y. (1982). Journal of Membrane Science 11, *297*.

Jacobs, E.P. (1980). "Design of a tubular reverse osmosis element"; M.Sc. thesis, University of Potchefstroom.

Jacobs, E.P. (1988). "Statistical and numerical techniques in the optimisation of membrane fabrication variables"; Ph.D. thesis, Institute of Polymer Science, University of Stellenbosch.

Jacobs, E.P.; Sanderson, R.D. and Botha, G.R. (1982). "Development of tubular membrane systems and modules"; final report to Water Research Commission, March 1982, University of Stellenbosch.

Jacobsen, M.K. (1985). "Manufacture of cheese from ultrafiltered milk"; North European Dairy Journal 2, *38*.

Johnson, J.S. (1986). "Materials for membranes"; Chemical Engineering, August 18, *121*.

Jonsson, G. (1985). "Moelcular weight cut-off curves for ultrafiltration membranes of varying pore sizes"; Desalination 53, *3*.

Kamide, K. and Manabe, S. (1985). "Role of microphase separation phenomena in the formation of porous polymeric media"; ACS Symp. Ser. (ACSMC) 269, Mater. Sci. Synth. Membr., *197*.

Kaszyski, M. (1980). "The role of UF in the production of ultra-high purity water"; Paper at 41st Proc. Int. Water Conference, Pennsylvania.

Kern, D.Q. (1950). in "Process Heat Transfer"; Mc Graw-Hill Kogakusha, International Student Edition, *132*.

Kesting, R.E. (1971). in "Synthetic Polymeric Membranes"; Mc Graw-Hill, N.Y.

Kesting, R.E. (1977). in "Reverse Osmosis and Synthetic Membranes. Theory, Technology, Engineering"; Ed. S. Sourirajan; National Research Council Canada Publications, Ottawa, Canada.

Kesting, R.E. (1985). "Phase inversion membranes"; ACS Symp. Ser. (ACSMC) 269, Mater. Sci. Synth. Membr., *131*.

Kirk, D.E.; Montgomery, M.W. and Kortekaas, M.G. (1983). "Clarification of pear juice by hollow fiber ultrafiltration"; Journal of Food Science, 48, *1663*.

Kuroda (1986). Chemical Abstract 104 : 71034r.

Lefebvre, M.S.; Fell, C.J.D.; Fane, A.G. and Waters, A.G. (1980). "Permeability parameters of a novel polyamide membrane" in Ultrafiltration Membranes and Applications; Ed. A.R. Cooper, Plenum, NY.

Lloyd, D.R. and Meluch, T.B. (1985). in "Materials Science of Synthetic Membranes"; Ed. D.R. Lloyd, American Chemical Society, Washington, D.C.

Loeb, S. and Sourirajan, S. (1962). Adv. Chem. Ser. 38, *117*.

Lonsdale, H.K. (1966). "Properties of Cellulose Acetate Membranes"; chapter 4 in Desalination by Reverse Osmosis, Ed. U. Merten, MIT Press, Cambridge, Mass.

Lonsdale, H.K. (1972). "Theory and practice of reverse osmosis and ultrafiltration" in Industrial processing with membranes, Eds. R.E. Lacey and S.Loeb, Wiley Interscience, NY.

Madsen, R.F.(1977). "Hyperfiltration and Ultrafiltration in Plate-and-Frame Systems"; Elsevier, Amsterdam.

Matthews, M.E. (1979). "Advances in whey processing-ultrafiltration and reverse osmosis"; New Zealand Journal of Dairy Science and Technology 14, *86*.

Maubois, J-L. (1984). "Recent developments of ultrafiltration in dairy industries"; paper presented at Europe-Japan congress on Membranes and Membrane Processes, Stresa, Italy.

McKinney, R. (1972). in "Reverse osmosis membrane research"; Eds. H.K. Lonsdale and H.E. Poddall, Plenum press, N.Y.

McKinney, R.; Hofferebert, W.L. and Carden, J.A. (1974). Separation and purification methods 3, *87*.

Merin, U. and Cheryan, M. (1980). Journal of Applied Polymer Science 25, *239*.

Michaels, A.S. (1968). "Ultrafiltration" in Progress in Separation and Purification, volume 1, Ed. E.S. Perry, Interscience, N.Y.

Nakao, S. and Kimura, S. (1981). "Analysis of solutes rejection in ultrafiltration"; Journal of Chemical Engineering of Japan 14(6), *32*.

Nakao, S.; Yumoto, S. and Kimura, S. (1982). "Analysis of rejection characteristics of macromolecular gel layer for low molecular weight solutes in ultrafiltration"; Journal of Chemical Engineering of Japan 15(6), *463*.

Nielsen, C-E. (1983). "Fining of apple juice by Ultrafiltration"; DDS rapport 1983-GB-0383-50.

Nishimura, M. (1977). Kobunshi Ronbunshu 34, *713*.

Nguyen, Q.T.; Aptel, P. and Neel, J. (1979). "Characterisation of ultrafiltration membranes part 1. Water and organic-solvent permeabilities"; Journal of Membrane Science 5, *235*.

Nguyen, Q.T. and Neel, J. (1983 a). "Characterisation of ultrafiltration membranes part 4. Influence of the deformation of macromolecular solutes on the transport through ultrafiltration membranes"; Journal of Membrane Science 14, *111*.

Nguyen, Q.T. and Neel, J. (1983 b). "Characterisation of ultrafiltration membranes part 3. Role of solvent media and conformational changes in ultrafiltration of synthetic polymers"; Journal of Membrane Science 14, *97*.

Paperfuss, H.D.; Gross, J.F. and Sanchez-Ruiz, F. (1978). "Application of boundary-layer theory to ultrafiltration through flat semipermeable membranes"; American Institute of Chemical Engineers Symposium Series 74, *218*.

Parret, T. (1982). Technology, March 1982, *16*.

Paulson, D.J.; Wilson, R.L. and Spatz, D.D. (1984). "Reverse osmosis and ultrafiltration applied to the processing of fruit juices"; paper presented at American Chemical Society National Meeting, Philadelphia.

Pepper, D. (1980). "Membrane Life, Capacity and Costs"; Desalination 35, *383*.

Pilnik, W. and Voragen, A.G.J. (1970). "Pectic substances and other uronides" in The Biochemistry of Fruits and their Products, Academic Press, London, England.

Porter, M.C. (1979). in "Handbook of Separation Techniques for Chemical Engineers"; Ed. P.A. Schweitzer, McGraw-Hill, N.Y.

Porter, M.C. (1981). in "Synthetic Membranes : Desalination"; volume 1, Ed. A.F. Turbak, American Chemical Society Symposium Series 153, Washington, D.C.

Rekers, C.J.N. and Gons, J. (1981). "Installatie-ontwerp voor industriele toepassingen van membraanfiltratie"; Polytechnisch Tijdschrift/Prosestechniek 36, no. 11, *586*.

Robertson, C.R. (1984). "Evaluation, analysis and prevention of the fouling of UF membranes by macrosolutes"; Dept. Chem. Eng. Stanford Univ., CA, Final report PB85-128668/XAD.

Rohm and Haas (1976). "Hollow fiber ultrafiltration : A new concept in water treatment"; technical brochure, September.

Ross, W.R. and Louw, J.M. (1987). "Monitoring and control of anaerobic digestion"; Water SA, volume 13, no. 4, *193*.

Ross,W.R.; de Villiers, H.A. and le Roux, J. (1988). "Sludge separation techniques in the anaerobic digestion of wine distillery waste"; Poster paper presented at 5th International Symposium on Anaerobic Digestion, Bologna, Italy, 22-26 May, 1988.

Saier, H.D. (1977). Chemie Labor Betr. 28, *6*.

Schwarz, H.H.; Bossin, E. and Fauter, D. (1982). Journal of Membrane Science 12, *101*.

Shen, J.S. and Probstein, R.F. (1977). Ind. Eng. Chem. Fundam. 16, *459*.

Smolders, C.A. and Vugteveen, E. (1985). "New characterisation methods for asymmetric ultrafiltratin membranes"; ACS Symp. Ser. (ACSMC) 269, Mater. Sci. Synth. Membr., *327*.

Spatz, D.D. and Friedlander, R.H. (1978). "Rating the chemical stability of U.C. RO/UF membrane materials"; Water and Sewage Works 2, *36*.

Strathmann, H. (1984). "Water and waste water treatment experience in Europe and Japan using ultrafiltration"; in Synthetic Membrane Processes, Fundamentals and water applications, Ed. G. Belfort, Academic Press.

Strathmann, H. (1985). "Production of microporous media by phase inversion processes"; ACS Symp. Ser. (ACSMC) 269, Mater. Sci. Synth. Membr., *165*.

Strohwald, H. (1987). "Concentration of apple and pear sludge by ultrafiltration"; Beverage Review, Supplement to Food Review, November, *23*.

Tang,T.L.; Boroughs, R.D. and Chu, T.J. (1981). Industrial Water Engineering, January/February, *18*.

Tragardh, G. (1985). "Characterisation methods for ultrafiltration membranes"; Desalination 53, *25*.

Tragardh, G. and Olund, K. (1986). "A method for characterisation of ultrafiltration membranes"; Desalination 58, *187*.

Tweddle, T.A.; Kutowy, O.; Thayer, W.L. and Sourirajan, S. (1983). "Polysulfone ultrafiltration membranes"; Ind. Eng. Chem. Prod. Res. Dev. 22, *320*.

Uijtenboogaart, G. (1982). in "Quality of Eggs"; Proceedings of the First European Symposium FSTA 14, *80120*.

Uragami, T.; Naito, Y. and Sugihara, M. (1981). Polymer Bulletin 4, *617*.

Venter, B.G. (1988). (South African Society of Dairy Technology, Irene, RSA) Personal communication.

Ventoza, T.P. and Lloyd, D.R. (1985). "Poly(ether sulfone) membranes for desalination : membrane preparation and characterisation"; Desalination 56, *381.*

Veyre, R. (1984). Le Lait 64, *261.*

Wafilin B.V. te Zwolle (1983). Dutch Patent No. 8104486

Wood, A.S. (1987). "There's good reason for all the action in aromatic sulfone polymers"; Modern Plastics International, March, *32.*

Wysocki, G. (1976). Chemical Technology 6, *285.*

Yasuda, H. and Tsai, J.T. (1974). "Pore size of microporous polymer membranes"; Journal of Applied Polymer Science 18, *805.*

Zsigmondy, R. and Carius, C. (1927). Chemische Berichte 60B, *1047.*