PREPARATION OF TOLERANT MEMBRANES

WRC Report

submitted to the Water Research Commission

by

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EXECUTIVE SUMMARY

1. BACKGROUND AND MOTIVATION

A concerted research and development programme, initiated in the early 1970s by the (then) Minister of Water Affairs and administered and directed first by the CSIR and then the Water Research Commission, has resulted in the emergence of South Africa as one of the ten leading nations in the field of water treatment technology; particularly in the field of membrane technology. Aspects of the programme have included the addressing of problems in the treatment of industrial effluents and municipal (domestic) waters, the recycling of water from effluents and wastes, and the purification of water for the supply of potable water.

The success of the R & D programme has been due largely to the multidisciplinary and collaborative nature of the work done at the Institute for Polymer Science, which has provided a sound and growing data base now available for the solution of many water-quality problems. One of the important developments which emerged from the programme was the founding, initially with WRC support, of the commercial membrane-manufacturing company MEMBRATEK, now known as ENVIG, and the membrane technology which has evolved has been applied, inter alia, on large scale to the recycling of water at SASOL and MONDI.

Despite the successes of the membrane technology R & D programme to date, there remains a continuing and growing need for further advances in this field.

Industries need improved and novel membranes for improved reduction of the salt content of effluents (i.e. zero-discharge applications), the reduction of the intake of valuable resource water by improving and increasing the recycling of water reclaimed from effluents, and the sterilization of water.

Municipalities require efficient water treatment means so as to be able to supply disinfected water, of good quality and in adequate quantities, for domestic use. Membrane systems, which purify, soften and decolourize water, can be used to meet these needs.

There is also a need to train and provide skilled membrane scientists to plan and operate the necessary membrane systems.

Significant advances in membrane technology will be made by the development of "tolerant" membranes (tolerant meaning resistant to fouling and chemical degradation by chlorine, ozone,

etc.). The "tolerant membranes" programme is therefore directed at the development of novel and robust membranes and procedures, for use by industry and municipalities. Use of such membranes will increase the range of membrane applications as they would be more tolerant to harsh feedwater conditions. This project supports the project on the development and design of prototype modules and plants of Dr. Ed Jacobs. The "tolerant membranes" programme will continue to operate in collaboration with other R & D bodies.

The motivations for the specific objectives listed below have been included in the results and discussion section (section 3).

2. OBJECTIVES

The objectives of the "tolerant membranes" project were based on the research and development of membranes which would meet the water and effluent-treatment needs of industry and municipalities. The initial objectives included:

1. To collaborate with industry and other research bodies, such as (a) with ENVIG in the development of a local composite tubular membrane module, (b) with Prof. D.F. Schneider (Organic Chemistry Department, University of Stellenbosch) in the synthesis of polyamides from furans, and (c) to be of assistance to Prof. G. Summers (VISTA) in the modification of polysulphone;

2. Regeneration of substandard and degraded CA membranes;

3. Studying of polyvinyl(alcohol)-based membranes for nanofiltration, their modification, characterization and evaluation as novel membrane materials;

4. Preparation of fluorinated microfilter membranes for ozone distribution in gas/water membrane contactors;

5. Preparation of hydrophilic polymer surfaces, gluable by epoxy and wettable by water.

Attention was also given to the following, as low-funded work:

6. Preparation of hollow-fibre carbon membranes;

7. Oxygenation and de-oxygenation of water by means of nonporous gas-separation membranes.

The latter two topics were included in two Ph.D. projects, funded by ESCOM and SASOL, respectively.

8. The preparation and publication of scientific papers, presentation of talks and posters at conferences and the compilation of yearly and final reports were to receive significant attention.

This final report comprises the following sub-reports.

Part 1: The preparation and evaluation of modified phenolics for the regeneration of sub-standard and degraded cellulose acetate membranes by as *in situ* treatment;

Part 2: Gas/water membrane contactors for ozonation;

Part 3: The modularization of thin-film composite membranes.

3. RESULTS AND CONCLUSIONS

3.1 Collaboration with industry and other research bodies

(a) Ultrathin film (UTF) composite tubular membranes, CAMOH 5, made from poly-2-vinylimidazoline (PVAM) and polyvinylalcohol (PVOH) and crosslinked with 3,5-dichlorosulphonylbenzoyl chloride (SCI), were fabricated and submitted to ENVIG for insertion in their locally developed tubular module. These modules did, however, not perform as well as the single tubular membranes did. Analysis of the single tubes after modularization revealed that, although a few tubes had poor rejection points, most membranes still appeared to be in good condition. Poor membrane module performance was thought to be due to module or modularization failure.

IPS therefore supplied further membranes to Membratek (now ENVIG) and assisted in their insertion into an ENVIG module with new rings. This module performed adequately, exhibiting a salt retention of 98% and a water flux of 33 ℓmh after 400 hours testing time (Feed solution: 2000 mg/ℓ NaCl, 20°C, 3 MPa). It was found that the UTF composite membrane is rather brittle and required very careful handling during insertion into modules, unlike the more robust CA membranes. It is now possible to successfully make an IPS UTF composite RO membrane in a local Membratek (ENVIG) module.

(b) The aromatic polyamides (aramids) are polymeric materials of high strength, chemical resistance and thermal stability and have been widely used in the field of membrane science, but their use in membrane manufacture is now an ageing technology. As relatively small amounts of membrane materials are required to fabricate large areas of membranes, more exotic materials can and should be considered for the making of improved membranes. When choosing novel membrane materials, the dependence of membrane properties on diffusion rates and solubility of water in the membrane polymer is a most important consideration. Improved membrane performance, especially in terms of higher fluxes, could be expected from membranes made from hydrophylic polymers. Furan is a highly polar, hydrophilic molecule and able to absorb much more water than Kevlar or Nomex are able to do.

The synthesis of furan-based membrane materials was therefore investigated.

Convenient and high yield syntheses were devised for furan-2,5-dicarboxylic acid, furan-2,5-dicarboryl chloride and dimethyl furan-2,5-dicarboxylate. These could all be used in polyamide synthesis, and various polymerization procedures were investigated to determine the most effective method of preparing high molecular mass membrane polymers. Five aramids, all structurally related to Nomex and Kevlar, were synthesized. The most suitable synthesis method included the use of thionyl chloride and N-methyl pyrrolidone as catalytic system, with additives. The molecular masses of the resulting aramids were, however, not considered as being high enough for use in commercial application. A detailed report on this work is described in the M.Sc. thesis of D. Stofberg "Synthesis of Polyamides from Monomers derived from Furfural", University of Stellenbosch (February 1995).

(c) Interaction with Prof. G. Summers of VISTA university, regarding the modification of polysulphone, has been established. Four students who studied the Polymer Honours course at the IPS are working on this topic with IPS assistance in terms of supplying relevant literature and polysulphone raw material. Polysulphone is being modified, according to the well-known methods of Guiver.

3.2 Preparation and application of supplemental polymer coatings for the regeneration of substandard and degraded CA membranes

Extensive research has been carried out into the synthesis, characterization and application of various polymeric coating materials to substandard and degraded cellulose acetate membranes, to improve their RO or NF performance. ESKOM and SASOL were originally interested in this area of research and in how the coatings may be used in their membrane operations. Membrane

regeneration can significantly reduce the need to replace substandard or degraded membranes, and the cost of production of recycled water.

Substandard cellulose acetate membranes were treated with various polymeric coating materials, such as resorcinol formaldehyde resins (RF), resorcinol-glutaraldehyde (RG) resins, tannic acid and poly(acrylic acid) (PAA). This was done either by dipping the membrane in an aqueous resin solution, or by *in situ* regeneration of the membrane in the membrane test rig.

The resorcinol-formaldehyde resins were prepared in various ratios of resorcinol to formaldehyde and characterized by electrospray mass spectrometry.

The effectiveness of the various resorcinol formaldehyde resins as coatings, to improve the RO performance of substandard membranes, were compared to the effectiveness of the acid treatments. Therefore, both the overall RO performance of coated membranes (salt retention and permeate flux) and the practical applicability of the regeneration procedure were taken into consideration.

It was established that both the resorcinol-formaldehyde resins and resorcinol-glutaraldehyde resins were effective in regenerating cellulose acetate (CA) RO membranes and that the former were also effective in regenerating CA UF membranes, both singly and in module form. On comparison of the various regeneration materials and processes investigated, it was found that all the treatments were equally capable of upgrading the performance of the CA RO membranes but that the *in situ* treatment process with resorcinol-formaldehyde resins was favoured. Partial and/or complete membrane restoration was achieved with RF resins for the regeneration of CA membranes. Increases in salt retention were, however, usually accompanied by some loss in permeate flux. The degree of performance improvement after membrane coating depends largely on the original membrane and its performance, e.g. **before** coating: (i) 60,1% R, (ii) 90,1% R; **after** coating (i) 91,4% R, (ii) 94,3% R.

Membrane regeneration can be effectively used to extend the useful lifetime of a CA membrane and reduce the cost of the production of recycled water. It was established, however, that a good physical and chemical cleaning regime is an essential pre-requisite for a successful regeneration procedure. A standard coating procedure is suggested (and described in the full report).

Progress in this area of the research has been very good and there is great scope for even further research and wider applications.

A detailed report on this work is described in the M.Sc. thesis of C.E. Morkel, "The Synthesis and Characterization of Reagents for Membranes", University of Stellenbosch, December (1996).

3.3 Poly(vinylalcohol)-based membranes

The study of poly(vinylalcohol)-based membranes, which included the chemical modification of PVOH, product analysis, application of products to membrane fabrication and eventual evaluation of membranes, has become a very large and difficult field of research. It has nonetheless been very widely and thoroughly studied and forms the basis of a Ph.D. project to be completed.

3.4 Preparation of fluorinated microfilter membranes for ozone distribution in gas/water membrane contactors

It is well known that it is becoming increasingly undesirable to treat raw water with chlorinating agents, because of the disadvantages of chloro-hydrocarbons. There has been a worldwide shift to alternatives such as ozone, peroxone, UV and chlorine dioxide. However, aspects of the ozonation process, e.g. rate of transfer of ozone to water, make it unattractive. The preparation and application of ozone contactor membranes, resistant to the strong oxidation potential of ozone, were investigated; these included polyvinylidene fluoride (PVDF) and surface-fluorinated PTFE (a "Teflon"-like material).

PVDF was successfully fluorinated and thoroughly analyzed. Surface tensions of untreated and fluorinated PVDF were determined.

PVDF capillary membranes were spun and the dried membranes were fluorinated. The membrane surfaces were analyzed by atomic force microscopy. It was seen that the PVDF capillary membranes were roughened during fluorination. It is, however, not yet known what effect this will have on ozonolysis through these membranes. Various studies need to be conducted to determine ozone production, but these have not yet been completed.

Protein absorption onto polysulphone, PVDF and fluorinated PVDF membranes was also determined. There was much less protein absorption of bovine serum albumin onto the fluorinated surfaces. This may be of significance in the creation of fouling-resistant membranes.

Studies on the mass transfer of ozone through the fluorinated membranes to waters of various qualities are continuing.

3.5 Modification of polypropylene surfaces

Polypropylene surfaces were modified to make them glueable with epoxies. This was done with the view of more easily housing membranes in modules. (The change to polypropylene modules

should be considered.) Polypropylene was successfully fluorinated, under the supervision of Atomic Energy Corporation personnel. The adhesion strengths of epoxy and fluorinated polypropylene surfaces were determined.

Assistance has been given to Hoechst in the USA with making their membranes more amenable to glueing for the manufacture of better modules. Polypropylene modules are the most widely used type of AKZO in Germany and Memtec in Australia. In South Africa it has not yet been decided by ENVIG whether they will consider producing capillary polypropylene modules.

In the short term the technology of modified propylene surfaces will be used to make pipes for household water distribution, with reduced levels of tainting, in local communities and for the making of crossflow modules for bioreactors.

3.6 Preparation of polyacrylonitrile and carbon membranes with ultraporous surfaces

Because of their high chemical, heat and radiation stability, high electrical conductivity and ease of control of porosity, amorphous carbon is a very popular adsorbent. It is, however, its fibre-forming nature which makes carbon superior to all mineral precursor materials for membrane production.

New ways of making hollow-fibre carbon membranes were investigated. High molecular mass polyacrylonitrile (PAN)-based copolymers were selected as precursor materials. Using a specially developed carbonization procedure, mechanically and chemically stable carbon membranes of a highly asymmetrical nature and with a wide range of pore sizes were produced. These membranes had excellent stability and strength and could be useful in bioreactors.

A detailed account of this research and its numerous conclusions has been described in the Ph.D. thesis of Mr. V.M. Linkov, "Preparation and applications of hollow-fibre carbon membranes", University of Stellenbosch, (December 1994). The researcher concerned has since left the Institute for Polymer Science for the University of Potchefstroom where he was instrumental in establishing the SASOL Centre for Separations Technology in the Chemistry Department. He is currently employed by the University of the Western Cape.

3.7 Oxygenation and de-oxygenation of water by means of nonporous gas-separation membranes

The development of thin gas-permeable polymeric membranes has stimulated research to evaluate their utilization for oxygen transfer to water.

The bubble-free oxygenation of water and wastewater by gas-permeable membranes is desirable for some applications in wastewater treatment, such as when the oxygen requirements are too high for conventional aeration systems, or when bubbling of air would result in the stripping of volatile organic compounds or foaming of industrial wastewater. It is also very important in the oxygenation of blood without denaturation of the blood.

The removal of oxygen from water is also important. A system for this process would have commercial value in the pretreatment of boiler feed-water and in the de-aeration of bottled beverages to improve shelf life. Degassing of water may be used in combination with groundwater oxygenation for *in situ* bio-remediation and in the manufacture of semiconductors.

The problems which have been studied earlier have concerned mainly membrane-water oxygenation-deoxygenation systems operating with porous membranes in the nonwetted (gas-field pores) mode. In general, the main problem associated with oxygenation-deoxygenation membrane water systems is the narrow range of the transmembrane pressure at which the process can be operated.

Studies of the problem of increasing the efficiency of the water-oxy(deoxy)genation membrane system by means of advanced module design and, simultaneously, by the use of highly permeable polymeric non-porous membranes were undertaken at the Institute for Polymer Science. In these studies a polyvinyltrimethylsilane (PVTMS) asymmetric membranes were used.

The following findings were made:

A new configuration for a membrane aerator was evaluated using non-porous PVTMS asymmetric membranes with the liquid flowing between the flat-sheet membranes along turbulence-promoter spacers. The oxygenation of water takes place without bubble formation. The rate of water deoxygenation with PVTMS membranes and vacuum pumping is effective and comparable with results obtained using a boiling technique. The use of asymmetric PVTMS membranes with a high selectivity factor for oxygen and nitrogen (α = 3,8) permits water to be more effectively oxygenated than by simple air bubbling when the liquid flow rate is high. The overall mass transfer coefficients

were found to be a function of water flow rate. The use of flowing water permits reduction of the boundary liquid layer resistance to oxygen penetration.

A mathematical model of a separation process in membrane-liquid contacting systems has also been developed. A pilot plant has been commissioned.

A detailed report of this work is included in the Ph.D. thesis of Mr. D.G. Bessarabov, "Microheterogeneous polymeric barriers for membrane contactors: Study of gas and vapour separations", University of Stellenbosch, (December 1996).

4. CONTRIBUTIONS AND RECOMMENDATIONS

The technology pertaining to the modularization of composite tubular membranes is now available to ENVIG, should they require it. The success in this field provides the opportunity and know-how to the modularization of any new membrane material within the factory context at ENVIG.

If in the implementation of these findings the industry requires or wishes to modify the membrane chemistry, new recommendations will arise in the future. Right now, the recommendation is to employ the skills developed in optimizing the new cross-flow module (1 year project approved).

The usefulness and significance of membrane regeneration technology has already been successfully applied and SASOL is interested in the large scale application. Further research and development is, however, necessary before membrane regeneration technology will be used in the initial production of NF membranes.

Research into fluorinated systems has gained application in the making of modules and results could form the basis of future bioreactor designs, water clarifiers and water distribution systems. Interest is increasing in "Teflon" capillaries for water-ozonisers for which there is a growing market for small scale units.

The oxygenation/deoxygenation technology has shown enormous promise, but changes in module design and enhancement by electrical driving forces will be a further logical extension of this exciting novel technology.

Manpower development aims of this programme were achieved and two of the students who participated in this programme are now full professors. Some ex-students have joined ESKOM and SASOL, spreading their technology and skills.

The impact of this project and its sister project on capillary membrane manufacture and application, under the leadership of Dr. Ed Jacobs, will make big inroads into drinking water provision for rural communities.

In recommendations for new research we have to take into regard the rapidity of research advancement versus the capabilities of industry to transfer the results of products and processes to the community.

Industry itself has certain needs, different to some of the research outputs. This scenario is similar to that of some communities who require even simpler drinking water provision technology than has been researched to date. The new research proposals take these ever-changing needs into account and, in future, much more attention will be paid to the use of solar power electricity, as power source, for newer low cost water treatment strategies using membranes.

New proposals

New proposals should include the use of solar heat to distill water. Successes have been achieved in this field (e.g. with the "rescue bag" and the low-cost solar still), but a further programme of prototyping is required prior to industrialization.

A second new proposal is to convert solar power to stored battery power and to use this to remove organic foulants from, and sterilize, drinking water.

A third proposal would be to use the abovementioned battery-stored solar power to remove salt ions from water on a continuous basis, with minimum requirements for maintenance and/or chemical additives.

Finally, the use of electronic devices for drinking water monitoring of colloids, organics and ions in a single process e.g. by electrochromatography, in the parts per million range down to the parts per billion range, should be considered.

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LIST OF ABBREVIATIONS

AFM	Atomic force microscope
°C	Degree celcius
CA	Cellulose acetate
CAMOH	Code for membranes based on PVAM, PVAL and SCI
CAMPIP	Code for membranes based on PVAM, PIP and SCI
cm	Centimetres
DMAc	Dimethyl acetamide
DMF	Dimethyl formamide
ESCA	Electron spectroscopy for chemical analysis
FTIR	Fourier transform infrared
g	Grams
g/ℓ	Grams per litre
h	Hours
kPa	Kilopascal
IPC	Isophthaloyl chloride
IPS	Institute for Polymer Science
K	Kelvin
ℓ	Litre
ℓmh	Litres per square metre per hour
mg/ℓ	Milligrams per litre
mm	Millimetres
MPa	Megapascal

m/s	Metres per second
NF	Nanofiltration
nm	Nanometre
PA	Polyamide
PAA	Poly(acrylic acid)
PAN	Polyacylonitrile
PCI	Patterson Candy International
PEG	Poly(ethyleneglycol)
PES	Polyether sulphone
PIP	Piperazine
PPIP	Code for membranes based on PVAL and PIP
PTFG	Poly(tetrafluoro ethylene)
PVAL	Poly(vinylalcohol)
PVAM	Poly(vinyl amidine) or (Poly-2-vinylimidazoline)
PVDF	Poly(vinylidene fluoride)
PVP	Poly(vinyl pyrollidone)
PVTMS	Poly(vinyltrimethylsilane)
% R	Percentage retention
RF	Resorcinol-formaldehyde
RG	Resorcinol-glutaraldehyde
RO	Reverse osmosis
s	Seconds
SCI	3-Chlorosulphonyl benzoyl chloride
SEM	Scanning electron microscopy

TEA	Triethanolamine
THF	Tetrahydrofuran
TSP	Trisodium orthophosphate
UF	Ultrafiltration
UTF	Ultra-thin film
UV	Ultraviolet light
XPS	X-ray photo electron spectroscopy

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PART 1

THE PREPARATION AND EVALUATION OF MODIFIED PHENOLICS FOR THE REGENERATION OF SUB-STANDARD AND DEGRADED CELLULOSE ACETATE MEMBRANES BY AN *IN SITU* TREATMENT

1. INTRODUCTION AND OBJECTIVES

The costs of membrane processes are largely governed by the frequency of membrane replacement. The usefulness of a membrane is characterized by the quantity of water of acceptable quality that it produces. The life of a membrane is often determined by the care with which the engineering and process environment of the new membrane is designed and operated. Mal-operation, often resulting from unfavourable feed conditions, results in membrane failure. This, together with the fact that cellulose acetate hydrolyses, results in the deterioration of cellulose acetate membranes. This usually leads to the requirement for membrane replacement, unless a suitable means of regenerating the membranes can be established. Membrane regeneration should extend the useful life of a membrane, thus saving costs in terms of membrane replacement.

The term "membrane regeneration" is usually associated with the acceptable restoration of the performance of spent membranes. This can be achieved in two different ways, namely: (i) by the cleaning the fouled membranes, and (ii) by coating substandard membranes. Whereas membranes cleaning is a subject which has been widely investigated, membrane coating has received little attention. This study was directed at the coating of membranes.

Various patents and publications describe the regeneration of deteriorated cellulose acetate membranes. The most well-known regenerants are synthetic polymers and tannic acid, which have been used effectively to improve the properties of deteriorated cellulose acetate membranes. Literature indicates that synthetic phenolics evolving from the natural phenolic derivative tannic acid, can act as regenerants which will have superior properties to those of natural tannic acid. To date, the regeneration capabilities of tannic acid and poly(acrylic acid) (PAA) have not yet been compared to those of resorcinol-formaldehyde (RF) resins, nor have the RF resins been characterized in terms of the effect of their molecular masses on their regeneration ability.

A systematic study of membrane treatment chemicals could be most valuable in the regeneration of substandard membranes, especially to lower membrane treatment costs and possibly to use technology spin-offs such as possible bactericidal properties.

This research project was undertaken to investigate the field of membrane regeneration with the following specific objectives in mind:

- synthesis of specific phenolics;
- characterization of these phenolics in terms of their molecular masses;
- application of these phenolics to substandard reverse osmosis membranes;
- application of these phenolics to nanofiltration membrane modules;
- evaluation and comparison of the RO and NF performance results of cellulose acetate reverse osmosis membranes treated with the abovementioned phenolics, with tannic acid and with poly(acrylic acid);
- the compilation of an effective standard method for the regeneration of substandard cellulose acetate membranes.

2. LITERATURE SURVEY: MEMBRANE REGENERATION

2.1 INTRODUCTION

A major factor that influences the cost of desalinating water by reverse osmosis is the cost of membrane replacement which corresponds to their useful life. The useful life of a membrane should relate to the quantity of water, of acceptable quality, which is produced by a membrane before its replacement becomes necessary. Membrane life is usually specified in terms of years of usefulness by the supplier. The reasons for the need to replace membranes arise from either a decrease in salt retention by the membrane, the loss of which may be due to hydrolysis, chemical reaction and/or minute mechanical defects, accompanied by an increase in water flux, or irreversible fouling of the membrane surface.

2.2 BACKGROUND STUDIES

Table 1.1 summarizes the developments in the regeneration of CA membranes.

Table 1.1: Development of CA Membrane Regeneration

Regenerant	Year	Description	References
Quaternary	1966	Desalination from tapwater higher than from distilled water	1, 2,
	1979	Retention: Before: 97% After: 99,31%	3
PVME	1969	Offered temporary improvement in salt retention	4, 5, 6, 7
	1970	Retention: Before: 97,48% After: 97,95%	8
	1979	Retention: Before: 96,91% After: 98,31%	3
Polyoxyethylene Nonylphenols	1970	High hydrophilicity: improved retention Low hydrophilicity: ineffective	8
Cationic Surfactants	1970	n-Alkyldimethylbenzylammoniumchloride improved salt retention	9
Anionic Surfactants	1970	Ineffective	8
Commercial Skin cleanser	1970	Salt retention: increased Flux: 20% decrease	8
Acetic Acid	1971	Retention: Before: 80% After: 98%	8
Polyelectrolytes	1973	2-poly(vinylpyridine), poly(vinylamine) used as dynamic membranes	9, 10
Aldehydes	1977	Retention: Before: 86,3% After: 97%	13
Vinyl Acetate Copolymers	1978	Polymeric Regenerant	14, 15
PVOH	1979 1988	Retention: Before: 96,04% After: 96,93%	3 16
CMC	1979 1988	Retention: Before: 93,94% After: 97,37%	3 16
Tannic Acid	1979 1988	Retention: Before: 96,16% After: 98,83%	3 16
PVP	1980	Retention: Before: 90,5% After: 97,5%	17
Resorcinol-Formaldehyde	1982	Retention: Increased Flux: Unchanged	18
Resorcinol	1983	Membranes dipped in resorcinol solution	19
Epoxy Resins	1986	Retention: Before: 98% After: 99,4%	20
Thermal Treatment	1987	Retention: Before: 75% After: 91%	21
NaCl solution		Membranes containing 55% water were dipped in a NaCl solution and contained 35% water afterwards	22, 23

In regeneration work performed at the Institute for Polymer Science, Stellenbosch and reported by Dalton *et al.* (1978) **[14, 15]**, cellulose acetate membranes were treated with vinyl acetate copolymers to improve their performance. Poly(vinyl acetate) (PVAc) was used because of its compatibility with cellulose acetate. Furthermore, copolymerization of PVAc with various organic acids, such as crotonic acid and maleic acid, improved the solubility of the copolymer in aqueous solutions at pH 9 to 10. Polyvalent cations such as cupric, zinc and aluminium were used to crosslink the polymers onto or into the membrane surface. Screening tests were performed on small membrane samples and on large RO-membrane modules. For the initial tests, membrane samples were immersed in a 1% solution of the appropriate polymer, removed after 30 min and then treated with a 0,5% cupric chloride solution for 30 min before they were rinsed and placed in the test cells. An *in situ* coating method was later adopted, as it was difficult to test membranes, remove them from the test cells, treat and then replace the membranes without causing damage to the membrane surface. A further advantage of this treatment was it could be applied in the field of operation.

Dalton *et al.* **[14, 15]** described the application of vinyl acetate and maleic anhydride-methyl-vinylether copolymer coatings to spent cellulose acetate desalination membranes which led to membranes with improved salt rejection properties but with an accompanying decrease in flux. The polymer coatings were applied to the membranes as aqueous solutions and were solubilized by lowering the pH, which resulted in crosslinking. Other copolymers such as poly(vinyl acetate-co-crotonic acid) and poly(vinyl acetate-co-exo-cis-3,6-Endoxo-Δ^4-tetrahydrophthalic anhydride) were also employed as coating materials for CA membranes. It was claimed that supplemental polymer coatings were a cheap and effective means for extending the useful lifetime of a membrane. They claimed further that, these coatings could increase membrane performance beyond what was possible by annealing alone. The results obtained for small membranes samples were better than those obtained for the spiral wound modules tested. They also stated that, in some cases, there were great differences between samples taken from sheet membranes and attributed this to the fact that the spiral wound membranes gave a performance which was an average performance for large sheets of commercial membranes.

During 1979 Guy *et al.* **[3]** under contract to the United States Department of the Interior, investigated a vast number of regenerants.

The Toyobo Company **[17-20]** in Japan is one of the companies that are currently actively involved in membrane regeneration. In 1980 **[17]** they patented the treatment of CA membranes with polyvinylpyrrolidone (PVP) as a method for increasing the retention by these membranes. A bundle of hollow fibre membranes made from cellulose acetate 27, HCHO 28 and acetone 45 parts, was set in a tubular pressure vessel and treated with an aqueous 0,8% PVP solution for 10 min. When a 2 000 ppm NaCl solution was passed

through the pressure vessel at 3 MPa, the water permeation rate and salt retention were 242 lmd and 97,5%, respectively, compared to 250 lmd and 90,5% for the untreated membranes. Patents granted to Toyobo in 1982 **[18]** and 1983 **[19]** disclosed the treatment of spent membranes with resorcinol and resorcinol-formaldehyde resins. The 1982 patent described the treatment of spent cellulose acetate membranes with 0,001% to 10% aqueous solutions of phenolic resin to restore the membranes. Thus, a hollow fibre with 97,5% salt retention was treated by circulating through it, for 2 hours at 40°C, a 0,01% aqueous solution of a phenolic resin of resorcinol 10, formaldehyde 12 and NaOH 0,4 mole, to restore the membrane to 99,2% salt retention while maintaining a water permeation rate similar to that of the original membrane. This retention was stable for more than 500 h. The 1983 patent described the treatment of spent cellulose triacetate hollow fibres by immersing the membrane into a 1% resorcinol solution for 16 h. The fibre was then rinsed and tested and an increase in salt retention from 98,54% to 99,86% was observed. Soaking in water did not improve the retention further. In 1986 **[20]** the Toyobo Company was granted a patent for the treatment of liquid separation membranes with an epoxy resin containing a curing agent. After a hollow fibre membrane had been treated with an epoxy resin and curing agent for 2 h at 40°C, the salt retention improved from 98% to 99,4% without a decrease in the water permeation rate.

The Daicel Company **[21]** in Japan patented the thermal treatment of CA membranes to restore the membrane performance. After the desalination efficiency of the membranes had decreased from 92% to 75%, the membranes were treated with hot water at 87°C. The retention of the membranes was increased to 91%.

The Development Centre for Seawater Desalination in China reported that various reagents, including CMC, PAA, modified poly(vinyl acetate) and tannic acid, could be successfully used for the regeneration of spent CA membranes.

2.3 MECHANISMS OF MEMBRANE REGENERATION

The mechanisms of membrane regeneration have been proposed by Subcasky **[7, 8]**. The theory of pore plugging has been proposed by Dalton *et al.* **[14, 15]**.

2.4 CONCLUSIONS

Table 2.1 indicates that there could be a chemical or physical association between the membrane and the regenerant and that the regenerants can be insolubilized upon changes in the feed conditions. This association is usually stable enough to maintain improved retentions. Regenerants that penetrate into the membrane pores without forming a surface skin on the membrane improve performance without significantly reducing product flux. The ideal regenerant should

- be inexpensive;
- associate with the damaged areas of the substrate membrane;
- be cured while adsorbed onto these areas of the membrane;
- comprise various particle or molecular sizes, or increase in size inside the membrane;
- tend to have a binding action on the water, so as to improve the sorption mechanism for water and exclude salt sorption.

Generally speaking, further advantages would be if the regenerant is:

- a simple chemical such as is often obtained in nature, being benign;
- a material which can be applied directly after manufacture or at a water production plant without needing to shut the plant down, and
- able to retard or inhibit further bacterial growth.

3. MATERIALS AND METHODS

3.1 SYNTHESIS OF RESORCINOL-FORMALDEHYDE RESINS

The synthesis and characterization of resorcinol-formaldehyde (RF) resins, including analysis by electrospray-mass spectrometry have been described in detail in the M.Sc.-thesis of C. Morkel **[24]** (Chapter 4). Several RF resins were prepared, with various R:F ratios (0,25:1-2,5:1).

3.2 RO MEMBRANE REGENERATION BY RF TREATMENT

3.2.1 Introduction

The Toyobo Company, Japan **[25]** found resorcinol formaldehyde (RF) resins to be effective in improving the performance of cellulose acetate (CA) RO membranes.

3.2.2 Membrane Treatment

The RO membranes investigated were:

- flat-sheet CA membrane samples from a damaged spiral wound RO module, and

- tubular RO membranes.

The membranes were treated in two ways, namely:

- *in situ* regeneration, or
- by dipping them into an aqueous resin solution.

3.2.2.1 *In situ Membrane Treatment*

Membrane samples were taken from the spent spiral wound RO module (Ref. 24, Chapter 5, Section 5.2.1), and fitted into the test cells. The membranes were then left for 1 h in which to stabilize, after which their RO performance was measured with a 2000 mg/ℓ NaCl solution. The membranes were then treated with a 50 ppm aqueous RF-x- or resorcinol-glutaraldehyde (RGx-solution) which was circulated through the test rig for 2 h at 40°C. After the system was cleaned, the RO performance of the membranes was tested with an aqueous 2 000 ppm NaCl solution (as described in Ref, 24, Chapter 5).

3.2.2.2 *Membrane Treatment by Dip-coating*

The membrane samples were immersed for 16 h into a 1% aqueous RFx resin solution. The excess resin was then rinsed off the surface of the membranes which were then inserted in the test rig. The membranes were left for 1 h in which to stabilize. The RO performance of the membranes was then determined as described above. Because of the nature of the test rig and the configuration of the test cells, it was not possible to test the RO performance of the dip-coated membranes prior to their regeneration. The performances of these membranes prior to regeneration were assumed to be comparable to those of the membrane samples that were treated *in situ*.

3.3 RO MEMBRANE REGENERATION BY ACID TREATMENT

3.3.1 Introduction

The treatment of sub-standard membranes with tannic acid and with poly(acrylic acid) (PAA) has been investigated earlier at the IPS as part of a project entitled "The development of fixed and dynamic membrane systems for the treatment of brackish water and effluents" and reported on in WRC Report No 219/1/94 **[26]**. It had been concluded that these acids could improve the separation properties of CA membranes. It was therefore decided to compare the performances of state-of-the-art acid-treated CA RO membranes with resorcinol-formaldehyde-resin-treated CA RO membranes.

3.3.2 Membrane Treatment

The method used to coat CA membranes with tannic acid and PAA was developed by Dr. Ed Jacobs at the Institute for the regeneration of spent CA membranes **[26]**.

Samples tested in these experiments were taken from a spent Filmtec membrane, described in Reference 24, Chapter 5 (section 5.2.1). The basic techniques adopted for the treatment of the CA RO membranes with tannic acid and PAA are described in Reference 24, pp. 74 and 78 respectively.

3.4 REGENERATION OF TUBULAR CA NANOFILTRATION MEMBRANES

RF 1.2 resins were used for the *in situ* treatment of tubular CA UF membranes as described in Reference 24, p. 84.

3.5 REGENERATION OF TUBULAR CA NF MEMBRANE MODULES

CA NF membranes were manufactured and housed in a re-usable PCI module at the Institute. The module was then installed and tested at the Uitenhage waterworks. The UF performance declined and module regeneration was considered. An attempt was made to regenerate the module in the field by using a pre-prepared resin formulation (RF1.2). The treatment was performed under conditions similar to those used in laboratory experiments (Reference 24, Chapter 6). The resin acted as a dosing chemical, rather than a regeneration chemical. Salt retention increased while the membranes were subjected to the resin treatment. As soon as the system had been cleaned and the resin removed from the feed solution, the UF retention returned to its value prior to treatment. Similar results were obtained when the treatment was repeated. The module was then returned to the Institute to be regenerated under laboratory conditions. When the module was sponge-ball cleaned, a fair amount of impurities was removed from the membrane-surface. This could probably have been the reason for the results observed during the first coating process (while in the field, the module had only been subjected to soap washes and not sponge-ball treatment). After the module had been washed, the performance of the module was again determined.

The module was then regenerated with a 50 ppm resorcinol-formaldehyde resin (R:F ratio 1.2).

(The performance of the module is tabulated later, in Table 1.7.)

4. RESULTS AND DISCUSSION

4.1 THE EFFECT OF RF AND RG COATINGS ON THE RO PERFORMANCES OF CA MEMBRANES

The RO performance results of a selection of *in situ* regenerated flat-sheet CA NF membranes with RF resins and a RG resin are shown in Table 1.2.

Table 1.2: RO performances of flat-sheet CA membranes regenerated with RF resins and a RG resin

Resin	Membrane No.	RO Performance			
		Retention (%)		Flux (lmh)	
		Before	After	Before	After
RFO.50	1	75,58	50,03	92,53	25,96
	2	86,04	33,89	92,69	28,75
	3	90,08	32,61	96,58	24,91
RFO.75	1	61,30	51,33	91,52	25,90
	2	73,08	41,37	92,22	27,55
	3	93,87	28,17	96,89	23,65
RG1.5	1	65,74	99,71	78,84	74,91

Partial and/or complete membrane restoration was obtained by utilizing Rfx resins for the regeneration of CA membranes. From Table 1.2 the different ranges of Rfx resins show that higher retention membranes gave better results with regenerants of lower molecular masses. The RFx resins were equally capable of regenerating the "more open" membranes. RFx resins were superior to the RG resin in regenerating a "more open" membrane.

The *in situ* coating process is much more practical than the dip-coating process and can be used during plant operation, i.e. it is not necessary to shut the entire plant down while

membranes are being regenerated. The *in situ* coating process is also less time-consuming than the dip-coating process and fewer chemicals are required for the regeneration process.

Coatings can be applied in succession, meaning that numerous coatings can be applied to a set of membranes until the desired improvement in membrane performance is obtained. The fact that excess coating material washes away from the surface in the dip-coating process was thought to be the cause of the increase in flux. This proved to be correct when an untreated membrane installed in the system showed an increase in retention (50% to 69%) and a decrease in flux (60 lmh to 44 lmh), and was thus regenerated by the excess coating material in the system.

The RO performance results of selected *in situ* regenerated tubular CA membranes, with a RF and a RG resin, are shown in Table 1.3.

Table 1.3: RO performances of two tubular CA membranes, regenerated with a RF and a RG resin

Resin	RO Performance			
	Before		After	
	Retention (%)	Flux (lmh)	Retention (%)	Flux (lmh)
RF1.2	96,72	15,01	98,70	13,07
RG1.2	96,86	15,36	97,67	13,57

From the experiments conducted on the tubular CA RO membranes, it was found that the treatment of the membranes with either the RF- or the RG-resins increased membrane retention. The increase in membrane performance was, however, larger after coating with the RF resin than with the RG resin. This was due to the molecular size of the regenerants. This led to the conclusion that lower molecular mass resins are required to treat membranes with a higher retention, having smaller defects in the surface structure, than membranes with a lower retention, as opposed to the large increase in performance which was obtained by treating a flat-sheet membrane with a RG resin. It would thus seem that the larger molecular size of the RG resin would be more suited to the regeneration of membranes with a lower retention.

4.2 THE EFFECT OF TANNIC ACID AND PAA COATINGS ON THE PERFORMANCES OF CA MEMBRANES

4.2.1 Tannic acid

Results obtained after the *in situ* regeneration of CA RO membranes with tannic acid are shown in Table 1.4.

Table 1.4: The effect of tannic acid treatment on CA RO membranes

Time (h)*	Flux (lmh)	Retention (%)
0	29,05	73,10
1	24,36	84,74
4	22,00	86,65
20	23,49	85,15
22	20,00	86,25
52	23,81	86,59
68	23,45	89,02
656	23,41	90,55
* See ref. 24		

4.2.2 Poly(acrylic acid)

Table 1.5: Regeneration of CA membranes by coating with poly(acrylic acid) and RFO.50

Time (h)	Flux (lmh)	Retention (%)	Comments
0	30,94	72,64	Before PAA treatment
9	26,52	83,58	
74	25,76	84,78	After PAA treatment
140	21,42	92,58	After RFO.50 treatment
187	21,42	89,45	
227	25,29	89,98	
552	25,15	89,95	

Coating with poly(acrylic acid) (see Table 1.5) did not result in sufficient improvement to regenerate the damaged cellulose acetate spiral membrane.

Results indicated that the first (PAA) and second (RF) coatings were incompatable, resulting in the second coating being washed off. It would therefore seem that the resorcinol formaldehyde resin coating cannot be successfully used as a coating on a membrane which had already been treated with PAA.

4.2.3 Comparison of RO performances of membranes treated with RFO.50, tannic acid and PAA

In Figure 1.1 a comparison is made in the regeneration of three sets of cellulose acetate membranes achieved by resorcinol-formaldehyde (RFO.50), tannic acid, and poly(acrylic acid) coatings.

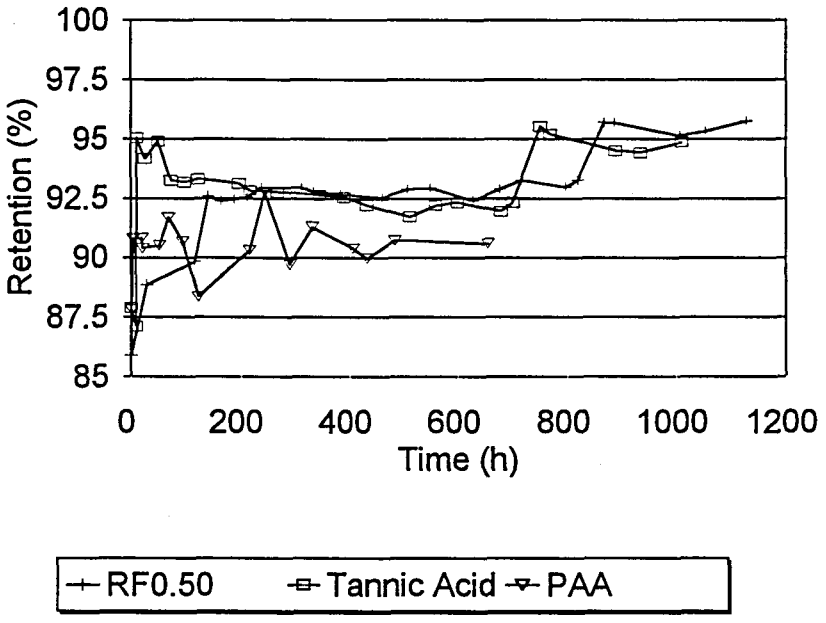

Figure 1.1: Comparison of RO performances of membranes treated with RFO.50, tannic acid and poly(acrylic acid)

There appeared to be little difference in the effectiveness of the various coatings, all coatings resulted in improved RO performances. The RF resin treatment was, however, superior to the other methods investigated in terms of the potential industrial applicability of the regeneration process. The RF regenerants could be applied *in situ*, thus offering a regeneration process which would not require the complete shutdown of the plant. The *in situ* process was also less time consuming than the other methods of regeneration investigated.

4.3 REGENERATION OF TUBULAR CA NANOFILTRATION MEMBRANES

Typical results for the regeneration of CA UF membranes with a RF 1.2 resin are shown in Table 1.6.

Table 1.6: The RO performance of tubular CA nanofiltration membranes coated with a RF 1.2 resin *in-situ*

	Sample 1		Sample 2	
Time (h)	Flux (lmh)	Retention (%)	Flux (lmh)	Retention (%)
0	35,81	44,57	34,71	45,74
7	23,93	71,84	23,20	72,69
115	25,98	66,28	25,12	67,25
232	26,75	64,86	25,84	65,8
400	27,56	62,89	26,59	64,11
616	28,07	62,56	27,56	63,63

Tests performed on dip-coated tubular nanofiltration membranes showed interesting results regarding the salt- and water permeability coefficients of the membranes, mapped on a log-log scale (Figure 1.2). The membrane performance first improved as expected (marker 30.1 to 30.2), but after some time there was a marked further improvement in the membrane performance (marker 30.3), after which the performance started to deteriorate and returned to its original state (marker 30.1). A possible explanation herefore is that the coating resin was washed off, or through, the membrane.

This non-linearity in performance behaviour might be an indication that the salt-retention mechanism in that region is no longer adequately described by the capillary-flow theory. This could be of great importance in the future development of regenerant materials and determination of fixation techniques.

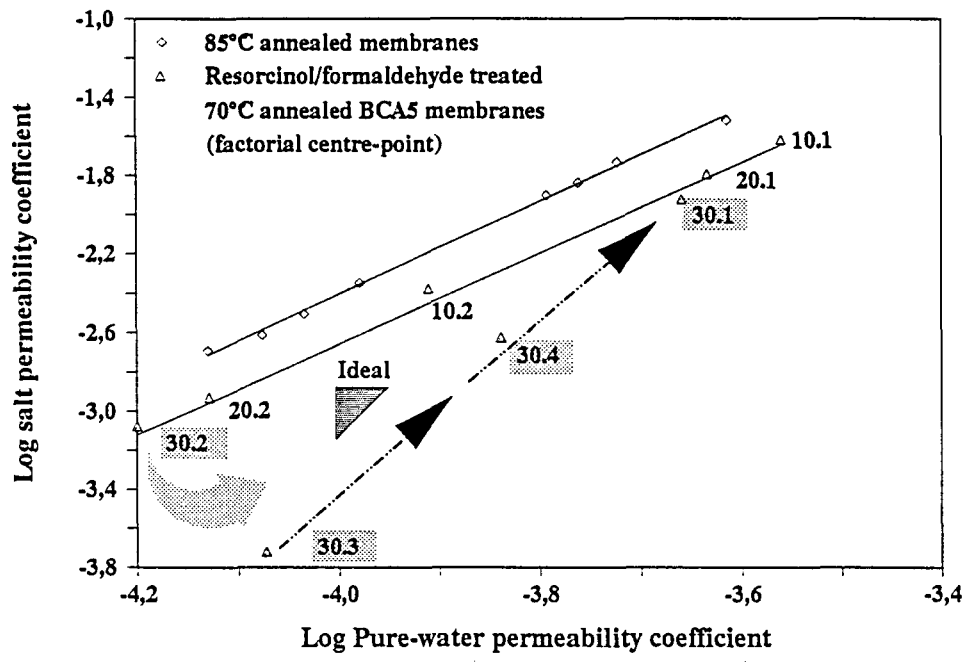

Figure 1.2: Performance of CA nanofiltration membranes dip-coated in a 1% RF1.2 solution

4.4 REGENERATION OF TUBULAR CA UF MEMBRANE MODULES

The membranes under consideration here were deteriorated membranes which had been in use at the Uitenhage waterworks.

Table 1.7: Performance of CA nanofiltration module (No. 3) after treatment with RF 1.2 (from Uitenhage waterworks)

Time (h)	Flux (lmh)	Retention (%)
0	30,77	35,27
7	26,87	42,45
72	29,08	44,31
115	28,69	40,49
783	27,22	39,89

The treatment of CA nanofiltration membranes with RF resins gradually improved the retention of these membranes, but also resulted in a decline in the flux. This was because the resins sealed the larger pores in the membrane skin structure, resulting in a greater hindrance of salt passage, without causing too large decrease in the water flux through the membranes. It can be said that CA nanofiltration membrane modules can be regenerated by using RF resins, but that there should be guarded against a too large increase in retention thus sacrificing flux through the membranes.

5. CONCLUSIONS

Resorcinol-formaldehyde resins were successfully prepared. These materials were then evaluated for their regeneration capabilities on cellulose acetate membranes. Resorcinol-glutaraldehyde, tannic acid and poly(acrylic acid) were also used as regenerants.

The various resorcinol formaldehyde resins (in terms of R:F ratios) showed that higher retention base membranes showed better improvements after coating when regenerants of lower molecular mass were used.

Both resorcinol-formaldehyde resins and resorcinol-gluteraldehyde resins were effective in regenerating cellulose acetate reverse osmosis membranes. The resorcinol-formaldehyde resins were also effective in regenerating tubular CA NF membranes, as well as tubular CA UF membrane modules.

The non-linearity in performance behaviour of tubular CA NF membranes coated with a RF 1.2 resin *in-situ* might be an indication that the salt-retention mechanism in that region is no longer adequately described by the capillary-flow theory. This could be important in the future development of regenerant materials and the determination of fixation techniques.

By comparing the different regeneration materials (regenerants) and the two coating processes it was concluded that all the treatments (regenerants) were equally capable of upgrading the performance of cellulose acetate membranes, but that the *in situ* treatment process with resorcinol-formaldehyde resins offers the following advantages:

- it is less time consuming than either dip-coating or acid treatment;
- it is easily applicable in the field of operation, not requiring plant shut-down, and
- less chemicals are required than for the dip-coating process

A suggested standard procedure for the regeneration of cellulose acetate membranes was proposed:

1. Prepare a resorcinol-formaldehyde resin by reacting 11 g resorcinol with 4,5 g formaldehyde in an aqueous solution of 100 ml H_2O for 4 h in the presence of a 10 ml 0,1 N NaOH catalyst;

2. Treat cellulose acetate membranes by adding a 50 ppm resin product to the feed stream for 2 h, while the feed stream is maintained at 40°C;

3. Clean the system and repeat the process if the desired retention has not yet been obtained by a single regeneration.

WARNING: A good physical and chemical cleaning regime is an essential prerequisite for a successful regeneration procedure. Refer to Appendix 1F of WRC Project 219 by Dr. Ed Jacobs, where washing with Biotex at pH 9,2 is recommended. A mechanical sponging of the surface is also recommended.

6. RECOMMENDATIONS

1. A systematic study of the bacterial attack on cellulose acetate membranes should be performed and the possible bacteriacidal activity of resorcinol-formaldehyde resins should be investigated.

2. The range of phenolics used could be broadened to include monomers with hydrophylic functional groups in the synthesis of coating resins.

3. Results of initial experiments on cellulose acetate nanofiltration membranes show a phenomenon that deviates from the capillary flow theory and will have to be investigated further. This could lead to either improved membrane manufacture, by adding the regenerant into the casting solution, or by improving the regeneration technique to improve the regeneration capability of these resins.

4. The cellulose acetate nanofiltration membranes have only been subjected to a few screening tests to see whether regeneration of these membranes is possible. In membrane regeneration it is always important to obtain a balance between permeate flux and salt retention, to develop a criterion for optimum membrane performance; one not merely based on maximum retention.

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PART 2

GAS/WATER MEMBRANE CONTACTORS FOR OZONATION (OZONE TRANSFER)

1. INTRODUCTION

1.1 Background to project, motivation and objectives

Many people in South Africa are living under Third World conditions. These people usually live in isolated smaller communities, in rural areas, where drinking water is often contaminated and diseases such as cholera and bilharzia are endemic. A solution to the problem of supplying good-quality drinking water to these communities is therefore very necessary. The building of large plants for water treatment is not always economically feasible.

Furthermore, the treatment of raw water with chlorinating agents often compounds the problem because of the formation of carcinogenic chloro-hydrocarbon substances. The worldwide shift to ozonation of raw water to avoid the formation of these toxic chemicals has solved some of these problems but, because of the inefficient transfer of ozone into water, extra costs and maintenance are needed to destroy the excess ozone. The bubble-through ozonation systems produce, in a given period, far more ozone than can really be transferred to the water; this also reduces the economy of the process. The main goal of this research project is to find an answer to most of the abovementioned problems.

In small-scale applications membrane contactors will offer a solution to the problems of: rate of ozonation, amount of ozone required and toxic gas emissions. Membrane contactors have very high surface-area-to-volume packing densities (about 1 000 m^2/m^3), and bubbleless ozonation can be achieved in such a contactor, which will operate on very much the same principle as commercially successful blood oxygenators do. It has already been shown that gas/liquid membrane contactors are about thirty times more efficient than conventional contactors, such as bubble columns, are.

The ozone water-disinfector would be operable with very little knowledge of the technical details of water purification. This would create the possibility of the

employment of "water-fiskale" or water-superintendents who could be appointed from the local community served. The only other important necessity for ozonolysis of water is electricity, which could be provided by a solar-energy generator in communities which do not have the regular ESCOM supply.

This simplified disinfecting equipment should be extremely well suited to the supply of potable water to smaller communities (less than 10 000 people). This does, however, not rule out the possibility of the future treatment of larger quantitites of raw water. The modular equipment can also be adapted to serve as an ozone reactor for treatment of municipal and industrial waste water with high organic content, and to provide a means of polishing secondary-treated domestic and industrial effluents. A further important product will be "Teflon"-like capillary membranes. This membrane could be used for gas-contacting/stripping and liquid-separating membrane systems in hazardous chemical environments such as the chemical, mining and water treatment industries.

The three main objectives of this project were:

- The creation of a gas/water (ozone/water) membrane contactor for ozonolysis of water;
- The creation of fluorinated (or "Teflon"-like) capillary membranes;
- The use of the fluorinated capillary membranes in an ozone/water contactor, to break down the toxicity of substances and improve the water quality (e.g. cleaning of industrial effluent and/or providing potable water from rural water supplies).

1.2 Chemical Background

1.2.1 Membrane material selection

Because of the highly corrosive nature of ozone towards most materials, the membrane material used should be chemically stable towards ozone. The polymer of choice should also be soluble in a variety of solvents, because preparing a membrane by the wet-phase inversion technique requires a homogeneous polymer solution which, upon contact with a non-solvent, phase-separates into a polymer-rich and polymer-poor phase. The material selected was poly(vinylidene fluoride) (PVDF) **(1)**. PVDF has the same basic chemical structure as polyethylene **(2)** but in the case of the former the two hydrogen atoms on every alternating carbon atom are replaced by two fluorine atoms.

(1) $-\left(CH_2-CF_2\right)_{n-}$ **(2)** $-\left(CH_2-CH_2\right)_{n-}$

Homopolymeric PVDF is, in general, chemically resistant to **[1]**:

- most acids
- salts and weak bases
- halogens
- halogenated solvents
- alcohols
- fluid or gas streams with temperatures exceeding 100°C
- nuclear and UV radiation
- strong oxidants

The reason for the greater chemical stability of fluoropolymers in general, and more specifically PVDF, is the high strength of the C-F bond (116 kcal), due to the high electronegativity of fluorine (χ = 4.10). In addition, the fluorine atom is larger than the hydrogen atom. This helps to shield the carbon backbone from attack, but it is still small enough to replace hydrogens without creating too excessive steric stresses in the molecule **[2]**.

PVDF is frequently used as a membrane material for separation operations.

1.2.2 Improvement of the chemical resistance of the PVDF membrane by surface fluorination

Although PVDF possesses many of the chemical-resistance properties of the perfluorinated polymers, e.g. "Teflon" or polytetrafluoroethylene (PTFE) **(3)**, it still lacks the almost total inertness of this group of polymers. The reason is that PVDF **(1)** still contains two hydrogen atoms per alternating carbon atom. The hydrogens are easily replaced, or attacked, by corrosive chemical agents. A technique was recently developed for the surface fluorination of polyolefins **[3]**. During surface fluorination, the polymer is brought into contact with fluorine gas or any other fluorinating agent. The hydrogen atoms in the first few layers of the surface of the polymer are replaced by fluorine atoms. Surface fluorination of the polymer therefore results in the formation of a fluorinated surface layer, while the bulk properties of the treated polymers are unaffected. The surface fluorination or PVDF membranes was studied.

(3) $-\left(CF_2 - CF_2\right)_{n-}$

This report will be divided into three main areas, each including experimental and results and discussion sections. These areas are:

- fluorination of PVDF, flat-sheet PVDF and fluorinated PVDF membranes (section 2);
- PVDF hollow-fibre capillary membrane manufacture (section 3);
- ozonation with hollow-fibre membrane contactors (section 4);
- study of other applications of fluorinated membranes (section 5).

2. PREPARATION OF FLUORINATED MICROFILTER MEMBRANES FOR OZONE TRANSFER (Fluorination of PVDF and flat-sheet membrane preparation)

2.1 Experimental

2.1.1 PVDF membrane preparation

Commercial PVDF ("Kynar 301F") was obtained from Pennwalt. Flat-sheet membranes were prepared by the phase-inversion process. A solution comprising 20% (by mass) of PVDF and 80% (by mass) N,N-dimethylacetamide was cast as a 200 µm-thick film on a glass plate. The film was precipitated by immersing the coated glass plate in water. The solvent was removed by leaching in water for 48 hours. The wet membrane was then dried in air for 48 hours.

2.1.2 Fluorination of PVDF membranes

Since, in previous studies, PVDF failed to react with a 10% mixture of fluorine in nitrogen, it was decided to expose the polymer, in membrane form, to the following fluorination conditions:

F_2 gas concentration	100%
Reactor pressure	100 kPa

Reaction temperature	50°C
Reaction time	4 h

2.2 Results and discussion

2.2.1 XPS analysis

XPS is based on the photoelectric effect and provides information about the chemical composition of surfaces. Binding energies of photoelectrons, emitted by ionization of the atoms with X-ray photons, are measured. The kinetic energy of these electrons depends on their binding energies, allowing the element that emits the photoelectrons to be identified.

Polyvinylidenefluoride samples were coated with a thin layer of gold and the 4 $f_{7/2}$ peak at 84 eV was used to correct for surface charging. The XPS spectrum of untreated PVDF is shown in Figure 2.1.

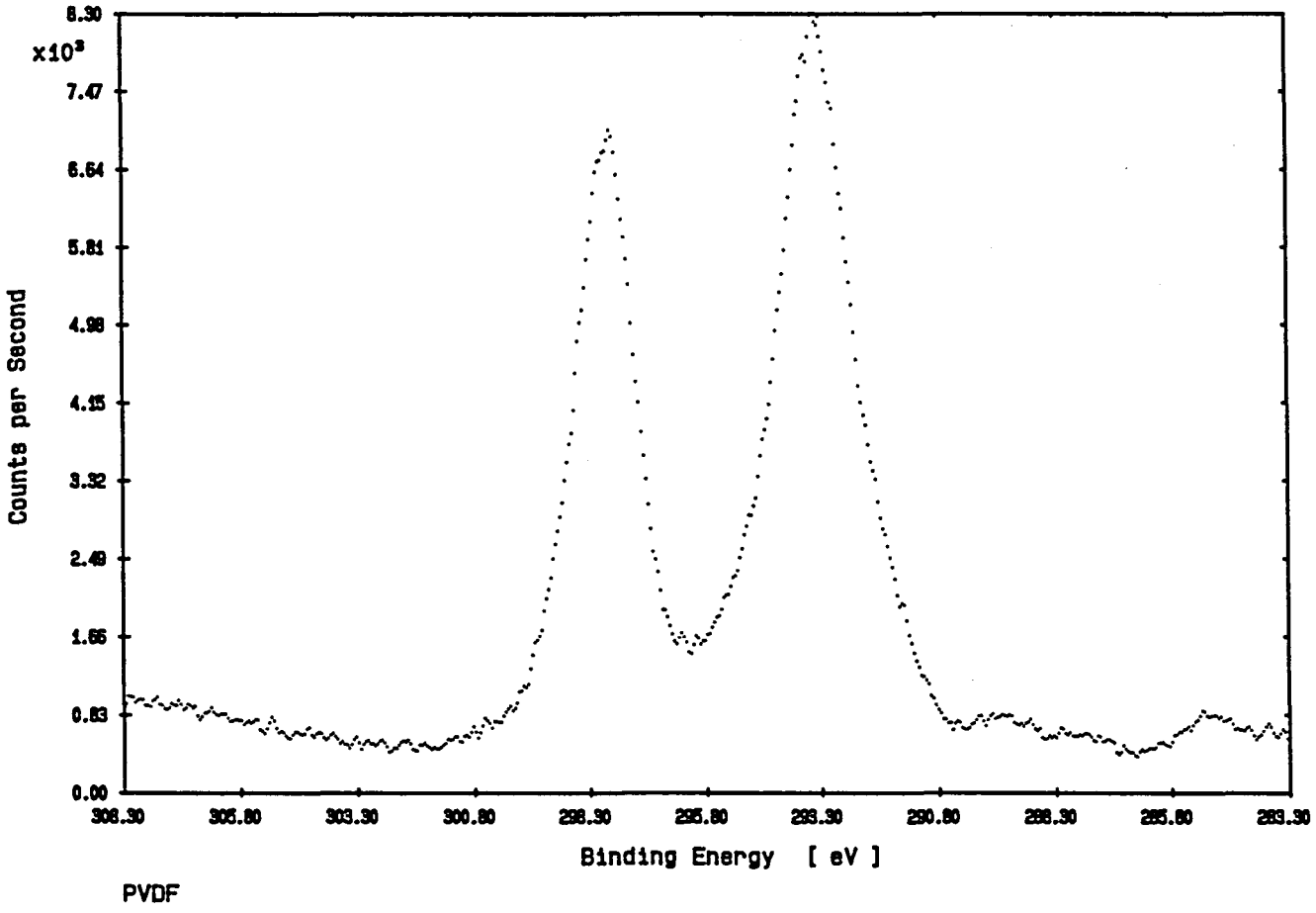


Figure 2.1: XPS-C1s spectrum of untreated PVDF

Two symmetric carbon peaks, at binding energies of 285,8 eV and 290,4 eV, represent the -C*H_2CF_2 and -CH_2C*F_2 structures, respectively.

Figure 2 shows clearly that surface fluorination changes the XPS spectrum of PVDF dramatically. The two separate peaks of PVDF are replaced by a complex spectrum of fluorinated units. Deconvolution (peak fitting) of the spectrum points to fluorinated PVDF having the following surface structural units:

284.9 eV	—C*H_2CH_2—
287.5 eV	—C*HFCH_2—
289.3 eV	—CH_2C*F_2—
290.1 eV	—CFHC*F_2—
291.4 eV	—CF_2CF_2—

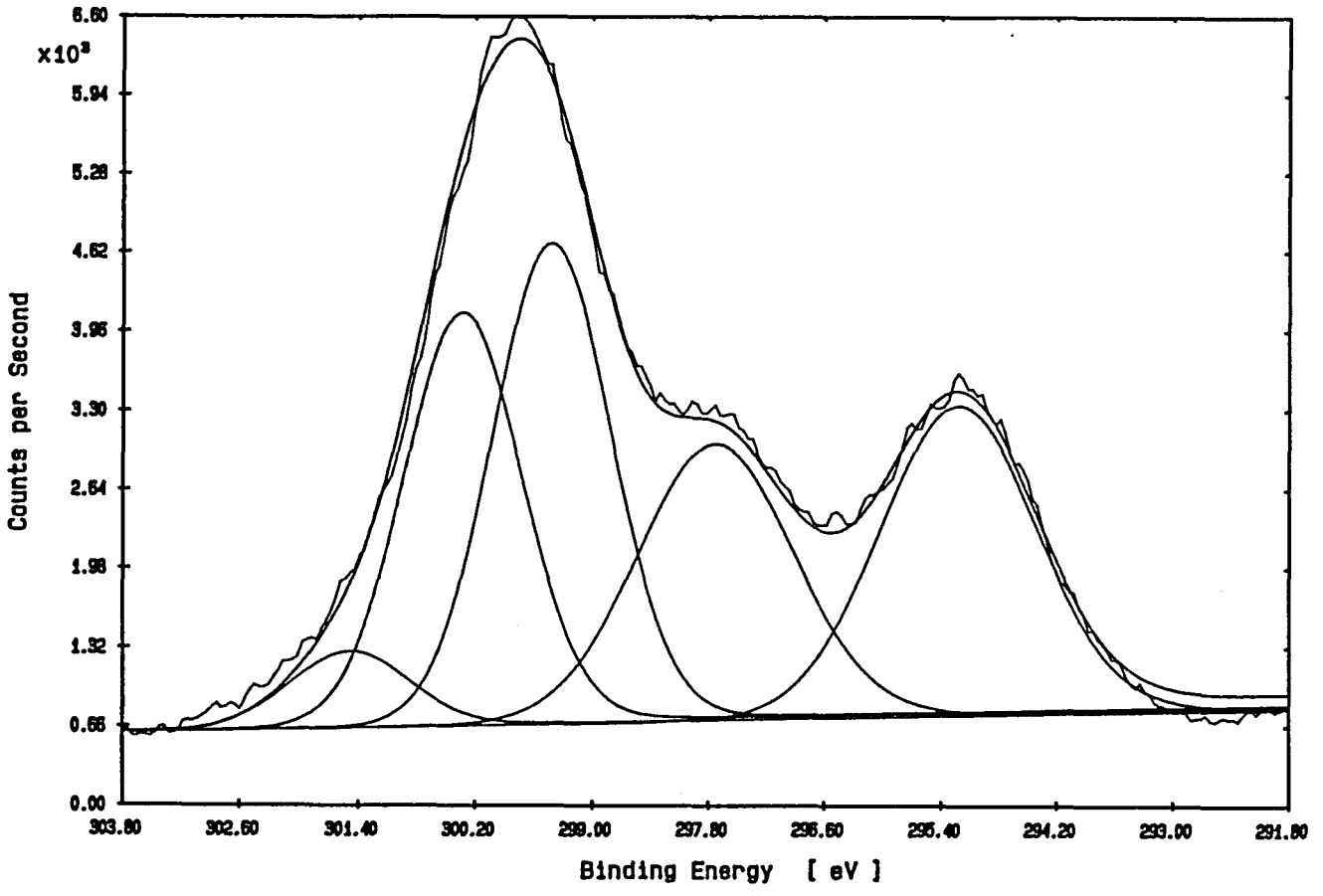


Figure 2.2: XPS-C1s spectrum of fluorinated PVDF

2.2.2 Surface energy studies

Contact angles of various test liquids on an untreated and on a fluorinated PVDF surface are presented in Table 2.1. Surface fluorination had a marked effect on the wettability of PVDF. The wettability of the PVDF by all the liquids used in this study, independent of the type of liquid used, was considerably decreased by adding additional fluorine atoms to the surface of PVDF.

Table 2.1: Contact angles of various test liquids on an untreated and on a fluorinated PVDF surface

Test liquid	Surface tension (mN m^{-1})	Untreated PVDF		Fluorinated PVDF	
	γL	θ_{adv}	θ_{rec}	θ_{adv}	θ_{rec}
octane	21,8	-	-	21,7	0
hexadecane	27,6	0	0	-	-
o-xylene	30,1	17,6	16,1	49,6	11,6
α-bromonaphtalene	44,6	52,6	44,2	78,6	8
methylene iodide	50,8	66,3	42,8	85,2	52,5
glycerol	63,4	79,3	23,6	104,7	11,8
water	72,8	90,9	12,7	113	45,7

The surface energy of a polymer or a surface can be determined by a Zisman plot. Zisman plots of the untreated and treated PVDF are shown in Figures 2.3 and 2.4, respectively. Problems were encountered with this method when liquids with an ability to form hydrogen bonds were used as test liquids. As discussed by Wu **[4]**, the plot through the contact angle values for water and glycerol is not linear, but curves towards higher values of cos θ. It is, however, evident from the curves in Figures 2.3 and 2.4 that fluorination resulted in the surface of PVDF resembling that of polytetrafluoroethylene, with the critical surface tension of wetting of the fluorinated samples reaching a value of below 20 mN m^{-1}, compared to 27,4 mN m^{-1} for the untreated polymer.

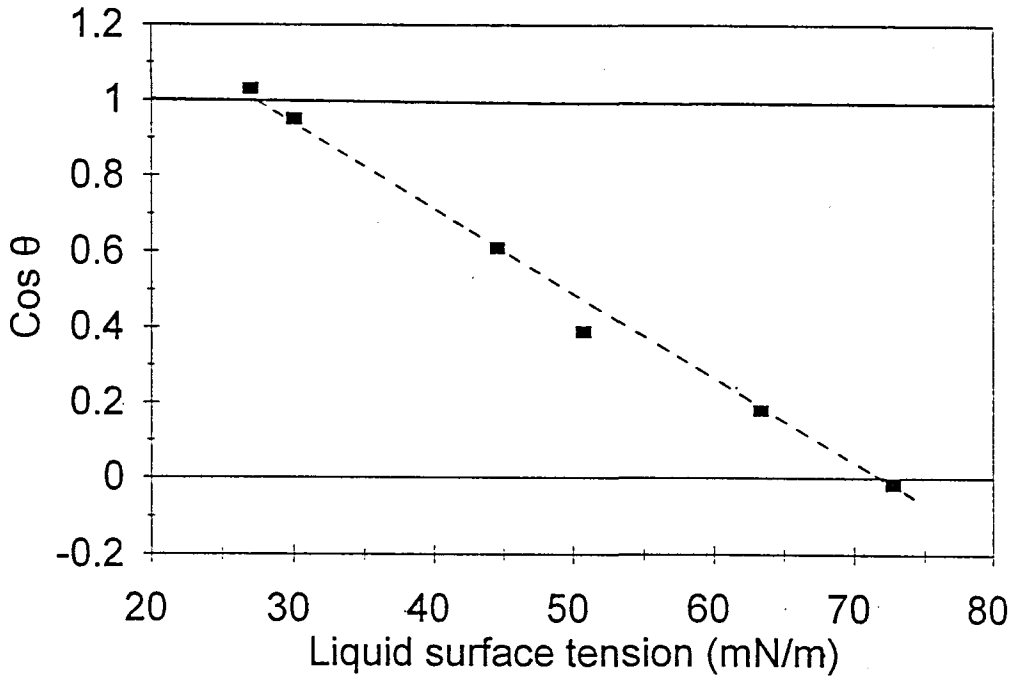


Figure 2.3: Zisman plot of untreated PVDF

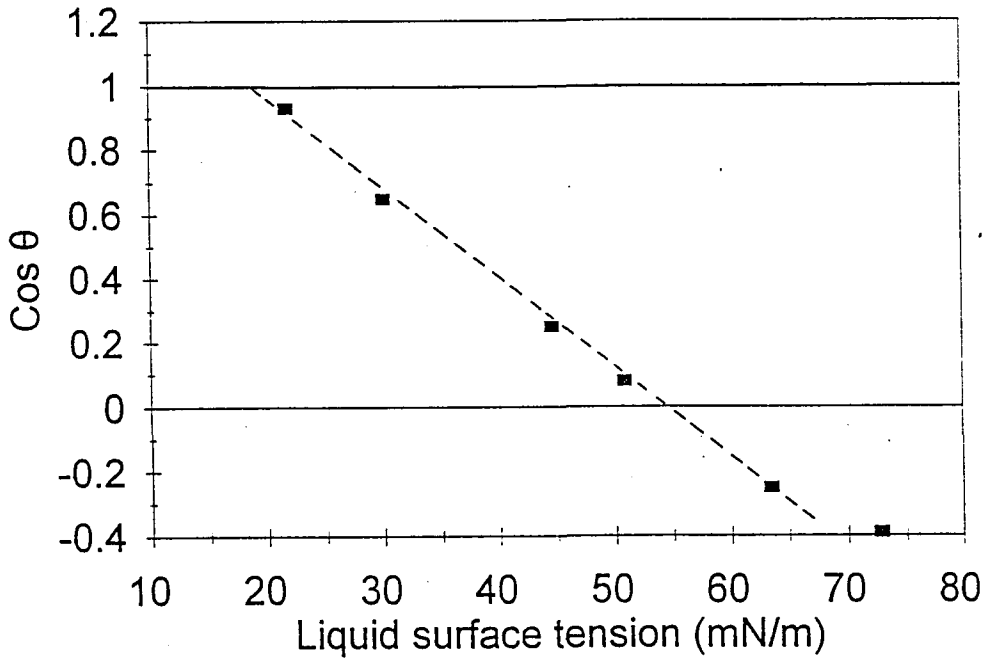


Figure 2.4: Zisman plot of fluorinated PVDF

During surface-tension studies of fluorinated polyethylene and fluorinated polypropylene, Zisman plots revealed an interesting phenomenon **[5]**. Unlike the untreated polymers, which exhibited single Zisman plots, the fluorinated polymers exhibited three distinct Zisman plots, according to the solvent type that was used. The surfaces obtained after the fluorination of polyethylene and polypropylene had lower non-polar and polar surface energies, but higher hydrogen-bonding surface energies than those of the untreated polymers. This phenomenon was attributed to impurities such as oxygen that were introduced into the fluorinated surfaces. The fact that only one Zisman plot was observed for fluorinated polyvinylidenefluoride indicated that oxygen, although always present as an impurity in commercial fluorine, was probably not introduced in the fluorination of this polymer, possibly because of steric hindrance.

Surface tensions of fluorinated and untreated PVDF are presented in Table 2.2. Surface tensions were determined by the geometric-mean method, developed by Owens and Wendt, and the harmonic mean approach of Wu **[4]**. In both these methods water was used as the polar liquid and methylene iodide as the non-polar liquid.

Table 2.2: Surface tensions of untreated and fluorinated PVDF

		Surface Tensions	
Method of determination	Polarity of wetting liquid	Untreated PVDF ($mN.m^{-1}$)	Fluorinated PVDF ($mN.m^{-1}$)
Geometric mean	non-polar	21,9	14,6
	polar	3,6	0,3
	total	25,5	14,9
Harmonic mean	non-polar	20,6	17,7
	polar	8,4	1,3
	total	29,0	19
Zisman	γ_c	27,4	17,2

Different surface tensions, as determined by the various techniques, were obtained for the same surface and the geometric-mean approach and gave very low values in both cases. The results obtained from both the harmonic mean and geometric-mean approaches, however, show that:

- surface fluorination lowers the surface tension of PVDF considerably;
- the polarity of the surface molecules is significantly reduced as the higher levels of fluorination cancel out the net of dipole-moments of the partially fluorinated PVDF; and
- the creation of articles from a readily processable polymer, having a surface that resembles the surface of PTFE, is possible.

2.2.3 Solubility of surface fluorinated PVDF

The solubilities of untreated and fluorinated polyvinylidenefluoride are compared in Table 2.3. PVDF readily dissolves in dimethylacetamide (DMAc), N-methyl pyrrolidone (NMP) and dimethyl formamide (DMF). Surface fluorination of PVDF rendered the polymer insoluble. This was an indication of the increase in chemical stability of polyvinylidenefluoride upon fluorination, a process in which treatment with fluorine gas resulted in a highly fluorinated surface.

Table 2.3: Solubility of fluorinated and untreated PVDF

PVDF Polymer	Dimethyl formamide	Dimethyl acetamide	N-methyl pyrrolidone
Untreated	soluble	soluble	soluble
Fluorinated	insoluble	insoluble	insoluble

2.4 Stability of fluorinated PVDF towards ozone

It is already known that PVDF is stable towards ozone at temperatures below 135°C. No significant corrosion is expected when fluorinated PVDF is exposed to ozone. The reason for this assumption is that fluorine gas [E° = 2,87 V], which is used to treat

PVDF, has a much larger oxidation potential [E°] than ozone does [E° = 2,07 V]. If PVDF can withstand fluorine it will also be resistant to ozone. Furthermore, in the case of the fluorinated PVDF material, there will be more carbon-fluorine bonds per molecule, a bond which is much stronger than the carbon-hydrogen bonds. The following techniques will be used to characterize both the PVDF and fluorination PVDF membranes for signs of corrosion:

- surface-sensitive techniques such as XPS, and contact-angle measurements;
- mass loss or increase;
- physical stability tests on membranes, during prolonged period of use;
- monitoring of the change in burst pressure and porosity of the membrane.

3. CONSIDERATIONS REGARDING PVDF HOLLOW-FIBRE CAPILLARY MEMBRANE MANUFACTURE

A literature study on PVDF capillary and hollow-fibre membrane formulations has been undertaken with special references to **PVDF membrane(s)** in either the hollow-fibre/capillary or any other form. There are several Japanese patents on this subject.

Several aspects of membrane manufacture were considered.

3.1 PVDF membrane drying

One of the key factors in successful capillary membrane manufacture is drying of the membrane. This is necessary because most of the potting materials used, e.g. epoxies and phenolics, require dry surfaces for effective adhesion. It is, however, difficult to dry the membrane without profoundly changing its physical properties and structure. The reason for this is that the capillary forces in a wet membrane are strong and drying destroys the structure of the fine pores, causing membrane shrinkage. Shrinkage of a membrane then causes a decrease in porosity and poresize of the membrane. Most of the drying methods are based on gradually changing the membrane casting solution solvents to solvents of much lower surface tension, until final drying of the membrane in a controlled atmosphere which is almost saturated with the solvent. Screening tests were carried out on both unsupported and supported PVDF membranes.

3.1.1 Drying of unsupported flatsheet membranes

3.1.1.1 *Experimental*

First, a screening test for drying wet flatsheet PVDF membranes was carried out. The amount of shrinkage of the membrane was used as a rough indicator of the change in membrane porosity and pore sizes during membrane drying. The membranes were soaked in various mixtures of methanol and water for certain periods of time, whereafter they were stored in a desiccator (see Table 2.1). After 3 days the membranes were still wet and shrank upon contact with air. In a second experiment, the desiccator tap was left open (see Table 2.2). The membranes dried much faster but shrank considerably.

Table 2.4: Procedure for drying flatsheet PVDF membranes with desiccator tap closed

Step	Drying procedure and membrane structure after drying	Duration
1	Soaked in CH_3OH/H_2O; 50:50	3 days
2	Soaked in CH_3OH/H_2O; 90:10	3 days
3	Dry in closed desiccator, saturated with MeOH.	3 days
Result: Membrane shrank after lid of desiccator was opened.		

Table 2.5: Procedure for drying flatsheet PVDF membranes with desiccator tap open

Step	Drying procedure and membrane structure after drying	Duration
1	Soaked in CH_3OH/H_2O; 50:50	3 days
2	Soaked in CH_3OH/H_2O; 90:10	3 days
3	Dry in dessicator with open tap.	3 days
Result: Membrane shrank considerably.		

After the solvent was changed from methanol to glycerol, a smooth, wrinkle-free membrane was obtained. The practical problem was that the membrane took a very long time (about a month) to dry (see Table 2.6). The glycerol also remained behind in the membrane and served as a plasticizer. This could possibly be a problem during subsequent fluorination of the membrane.

Table 2.6: Procedure for drying flatsheet membranes, using glycerol as the alcohol

Step	Drying procedure and membrane structure after drying	Duration
1	Soaked in glycerol/H_2O; 50:50	1 day
2	Dry in desiccator at first, then in direct atmosphere.	1 month
Result: Slow drying. Dried to smooth finish without too much shrinking. Glycerol remained in membrane.		

From the above it was deduced that an extra step was needed during which the alcohol solvent could be exchanged with a solvent which had an even lower surface tension and a higher vapour pressure than the alcohols. Hexane was selected. Table 2.7 shows the various treatments which were tried, using hexane as the last solvent before final drying. Much less shrinkage and fewer wrinkles resulted, compared with the results obtained when drying only with methanol.

Table 2.7: Various sequences for drying flatsheet membranes with hexane

	Sequence followed (Six hours duration for every sequence)				
Lot no.	CH_3OH/H_2O 50:50	CH_3OH	Hexane	H_2O 60°C	Dessicator
a	1	2	3		4
b		1	2		3
c	2	3	4	1	5
d			3	1	4

It was also found that by replacing the methanol with propanol, the resultant membrane dried with less shrinkage and fewer wrinkles.

3.1.1.2 *Results and discussion*

From the results of screening tests, the following steps for a drying protocol were suggested:

(i) Water should be substituted with a less polar solvent such as an alcohol, which should preferably have an intermediate boiling point (70-80°C) and volatility. As choice of alcohols, propanol was favoured above methanol and propanol was favoured above glycerol.

(ii) The alcohol should be substituted with a solvent of low surface tension, such as hexane.

3.1.2 Drying of supported flatsheet membranes

The shrinking of a membrane on a macroscopic scale, as witnessed in the abovementioned tests, is probably due to changes, on a microscopic scale, in the pore structure and porosity . It was therefore decided to use an alternate test procedure, which was based on evaluation of the pure water volume fluxes of the dried membranes. The relationship of a membrane's volume flux to its porosity and pore radius is described as a first approximation by the Hagen-Poiseuille's law **[5]**.

$$J_v = \frac{\varpi r^2}{8\eta\tau} \bullet \frac{\Delta p}{\Delta z} \qquad \textbf{(4)}$$

Where ϖ is the membrane porosity, r is the pore radius, η is the dynamic viscosity, τ is the tortuosity factor, Δp is the pressure difference across the membrane and Δz is the membrane thickness. From this it can be deduced that at constant $\Delta P, \Delta z, \eta$ and τ, the difference in pure-water volume flux (J_v) from one membrane to another is directly related to the membrane porosity (ϖ) and pore size (r). Hence, if the flux volume decreases, either porosity or pore size or both, must decrease. Thus, by comparing the volume fluxes of differently dried membranes, a picture of the changing pore structure and porosity during drying may be obtained.

3.1.2.1 *Experimental*

The membranes were cast from a 20% DMAc solution of PVDF ("Pennwalt 4000 HD"). A 300-micron-thick liquid film of this solution was spread on a polyester support, using a casting knife. The membranes were formed by precipitation and subsequent immersion in water at 20°C, then cut into smaller sections. One half of each section was used as a control and kept wet. The other half was dried by using the various drying procedures as described in Table 2.8. The corresponding dry and wet membranes were coded from M_1.3.1. to -5 (see Table 8). The D or N suffixes denote whether the membranes were dried (D) or kept wet (N). Each drying listed was of at least 24 hours duration. In all the cases, except in that of M_1.3.1.4.D, the membranes were finally dried inside a desiccator, the atmosphere of which was saturated with the last solvent listed in the protocol.

Table 2.8: Sequence of drying supported flatsheet PVDF membranes

Drying sequence (Drying steps were 24 h long.)						
Membrane code	Freeze Dry	H_2O : 2-Propanol 50:50	2-Propanol 100%	Hexane : 2-Propanol 50 : 50	Hexane 100%	Air Dry
M_1.3.1.D	1					1
M_1.3.2.D						
M_1.3.3.D		1	2	3	4	
M_1.3.4.D			1		2	
M_1.3.5D			1	2	3	

The initial pure-water fluxes of the dried membranes served as a measure of the amount of shrinkage of the membrane structures. High shrinkage is expected to result in a densifying of the membrane structure and a decrease in the pure water flux.

The membranes were tested on a flatsheet rig with a feed of RO water (conductivity 0,02 mS), at a pressure of 300 kPa and a flowrate of 2 ℓ/min at the feed side. Average values for the permeate fluxes of four membrane samples were recorded.

3.1.2.2 *Results and discussion*

The dried membranes were almost completely impermeable to water under 600 kPa feed pressure if they received no further treatment. Higher pressures would damage the membranes. The dried membranes were therefore re-wetted, before testing, by immersion in 2-propanol for 6 hours. The 2-propanol was the leached out with water

for another 6 hours. To determine the influence of the alcohol re-wetting step, wet membrane M.1.3.6.N (from the same section as M_1.3.1.N) was also subjected to the same immersion and leaching steps as for the dry membranes. Table 2.9 shows the results of pure-water volume fluxes of the dried and wet membranes. Time elapsed was taken as the time after the membrane was exposed to the pressurized feedwater.

Table 2.9: Volume fluxes of wet and dried PVDF membranes

		Average Volume Fluxes ($l.m^{-2}.h^{-1}$)		
Testing time elapsed (minutes)		10	20	30
Dry/Wet	Membrane code			
Wet	M_1.3.1.N	106	92	-
Wet	M_1.3.2.N	91	102	-
Wet	M_1.3.3.N	90	89	-
Wet	M_1.3.4.N	90	88	-
Wet	M_1.3.5.N	90	88	-
Wet membrane immersed in 2-propanol				
Wet	M_1.3.6.D	97	92	89
Dry	M_1.3.1.D	164	155	153
Dry	M_1.3.2.D	131	115	106
Dry	M_1.3.3.D	129	119	113
Dry	M_1.3.4.D	133	123	116
Dry	M_1.3.5.D	130	121	113

The percentage flux reduction or increase $(\Delta J_v\%)$ during drying was determined by

$$\Delta J_v\% = \frac{J_{v-dry} - J_{v-wet}}{J_{v-wet}} x\,100 \qquad (5)$$

where J_{v-dry} and J_{v-wet} are the volume fluxes respectively of the dry and wet membranes of the same section (see Table 2.10).

Table 2.10: Percentage change (% increase) in volume flux ($\Delta J_v\%$) upon drying

	Percentage change in volume flux (%)	
Time elapsed (minutes)	10	20
Membrane code		
M_1.3.1.D/N	74	68
M_1.3.2.D/N	23	12
M_1.3.3.D/N	41	33
M_1.3.4.D/N	47	38
M_1.3.5.D/N	45	37
Average	45	37

The membrane flux increased upon drying the membranes. An explanation for this unexpected behaviour is not possible at this stage.

The influence of rewetting of the dry membranes with 2-propanol on variation in flux was determined by comparing membrane M_1.3.6.N with membrane M_1.3.1.N. The former was a wet membrane, subjected to the same re-wetting and leaching procedures as the dried membrane. The highest increase in volume flux (from 94 to 164 $1.m.^{-2}.h^{-1}$, 74%, after 10 minutes) occurred with the freeze-dried membrane

M_1.3.1.D. The lowest increase in volume flux (from 106 to 131 $\ell.m^{-2}.h^{-1}$, 23%, after 10 minutes) occurred with the air-dried membrane M_1.3.2.D. The solvent-dried membranes exhibited a typical increase in flux of about 44%, from 90,6 $\ell.m^{-2}.h^{-1}$ to 130,73 $\ell.m^{-2}.h^{-1}$.

The results of these experiments indicated that these methods of membrane drying were impractical and offered little success. In future experiments, membranes would be dried in a manner similar to that described by other researchers **[6]**.

3.2 Solvent system selection

Capillary membranes were first cast from casting solutions containing hydrophilic pore-former additives such as poly(ethylene glycol) (PEG) and poly(vinylpyrrolidone) (PVP). Electronmicrographs of a cross-section of such a capillary membrane clearly showed the formation of a skin on both sides of the capillary (see electronmicrographs 1-2). There was also formation of finger-like voids which extended from both sides of the membrane into the middle. For the purposes of our work, it was preferable not to use hydrophilic pore-formers because of the likelihood of some remaining in the membrane after fabrication, causing the membrane to be hydrophilic; hydrophilicity of a surface is a property which is undesirable for gas-liquid contacting work. A further reason was that it is was unknown what the effect of the presence of such a material would have on the membrane material during fluorination. Therefore, the effect of fluorination on pure PVDF membranes was to be studied first, and only later would the effect be investigated of hydrophilic pore-formers in the membrane base material on membrane fluorination and gas/liquid contacting work.

3.2.1 Experimental

Of the eight well-known solvents for PVDF, three were selected for further study, namely: DMAc, NMP, DMF. A screening test was done to determine the approximate maximum PVDF polymer concentration achievable in homogeneous solutions of these three solvents. The PVDF polymer, obtained from Attochem in France, was the Foraflon 1000HD and 4000HD grades. The solubilities were determined, beginning with a 35% (by mass) solution of the polymer (of both grades) and gradually diluting the solution until the polymer grades were completely dissolved.

3.2.2 Results

It was found that the required polymer concentration for a casting solution for PVDF capillary membrane manufacture had to be between 20 and 30% (by mass) for both grades of PVDF polymer.

3.3 Spinning of capillary membranes

Figure 2.5 shows the apparatus used for the fabrication of capillary membranes. A 27,5% solution of PVDF, "Foraflon 1000HD" grade, dissolved in DMAc, was forced under air pressure through a ring orifice. The polymer solution was coagulated in a water bath. The inside of the capillary was coagulated with water as the core liquid. The fibre was drawn through the water bath at a constant speed with a series of rollers, during which time the polymer gelled completely. The excess solvent was removed from the membrane by leaching in water for 48 h. The membrane was dried by first exchanging the water with methanol, and then the methanol with hexane. The membranes were then dried in a controlled atmosphere for 5 days.

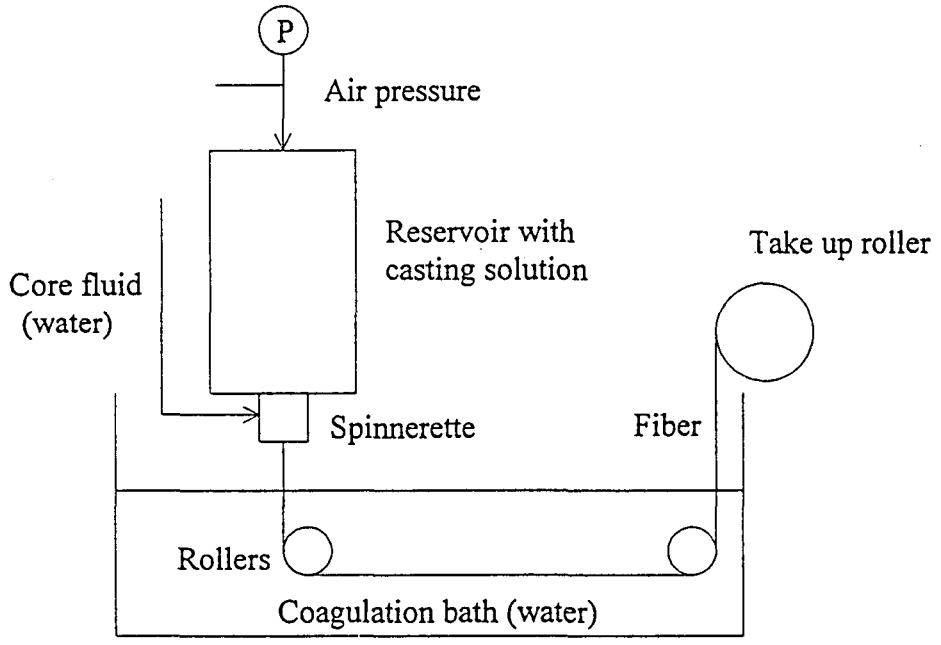


Figure 2.5: Spinning apparatus for capillary membrane fabrication

3.4 Membrane morphology

The spun fibre has an outside and an inside skin. Electronmicrographs of this membrane showed clearly that the bulk membrane phase consisted of a network of strands of polymer and voids, with no fingerlike structures or voids.

3.5 Membrane fluorination

The dry PVDF capillary membranes were fluorinated as previously for the flatsheet membrane (see section 2.1.2). The fluorinated membrane showed the same solvent resistance as noted previously (section 2.2.3). These membranes have yet to be characterized and this will be done as previously for the PVDF flatsheet membrane, using XPS, contact-angle measurements, surface-tension calculations, FTIR-Dynamic Mechanical Analysis, etc.

3.6 Characterization of fluorinated membranes

3.6.1 *Solubility*

The fluorinated membrane showed the same solvent resistance as previously described in section 2.2.3.

3.6.2 *Study of surface roughening with Atomic Force Microscopy*

It is expected that surface fluorination of a membrane will result in a change in the roughness of the membrane surface. Surface roughness is important as it has an impact on certain properties of the membrane, including the values of contact angles and membrane surface tension. While SEM-micrographs recorded at a magnifying power of 10^6 provided adequate information about the membrane morphology, surface roughening effects could not be easily determined. Atomic force microscopy (AFM) has a magnifying power of 10^9, offering resolution on a nanometre scale. Atomic force microscopy is based on the principle of the scanning of a single crystal or tip, connected to the end of a cantilever, closely over the surface of a specimen. The scan distance of the tip from the surface is in the region of van der Waal's radius distances. Hence, the tip is subjected to forces of attraction or repulsion, deflecting the end of a cantilever. By detecting the deflection of the cantilever, images of the topography of the surface can be formed.

Atomic Force Microscope. The AFM apparatus used was a TMX 2000 Explorer SPM System from Topometrix, Santa Clara, CA. It is capable of scanning an area of up to 1 μm x 1 μm in size. The tip for imaging is made of microfabricated silicon nitride (Si_3N_4). The SuperTip™ for enhanced performance was used. It is attached to a 130-μm cantilever with a certain force constant. The deflection of the cantilever is monitored by the deflection of a laser beam, reflected behind the cantilever, which is detected by a photodetector. Further details of the instrumentation are described elsewhere **[7, 8]**.

All AFM measurements were done under ambient conditions at 200 x 200 lines resolution, in varying height and constant force mode. The *z*-feedback circuit adjusts the *z*-position of the sample keeping the deflection of the cantilever constant, while scanning the sample in the *x* and *y* directions.

3.6.2.1 *Experimental*

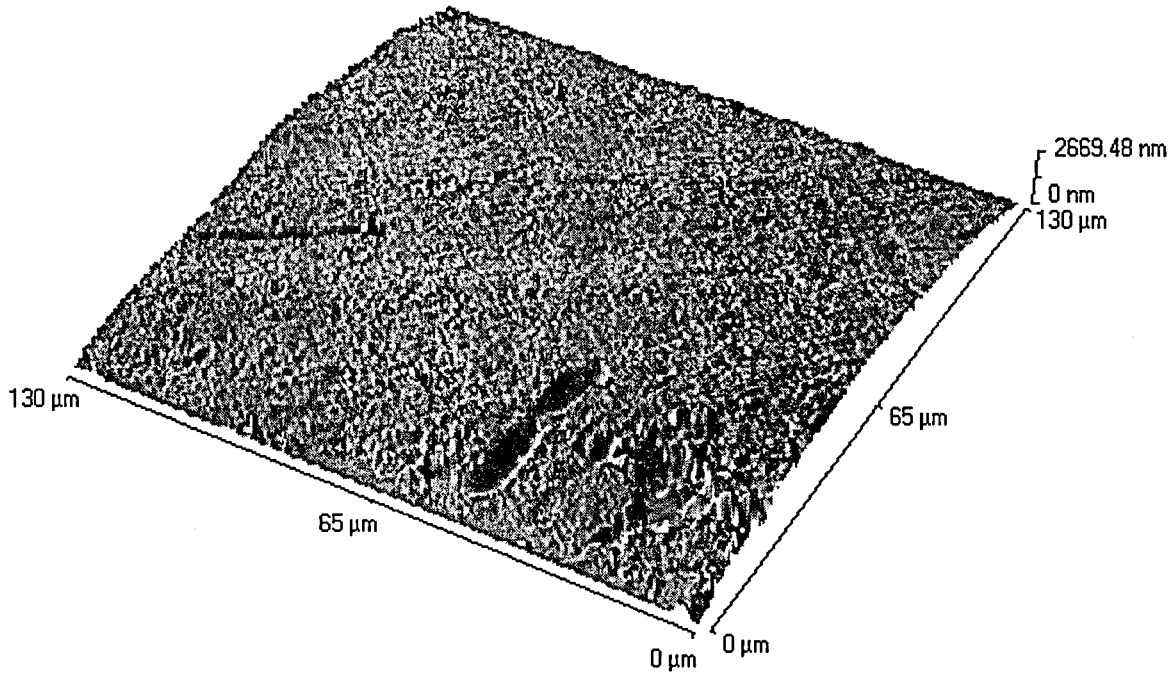
Specimen preparation. Specimens of PVDF and fluorinated PVDF capillary membranes were randomly selected. Three specimens of each type of membrane were fixed onto a flat metal plate with an epoxy. Several images of each sample were recorded.

3.6.2.2 *Results and discussion*

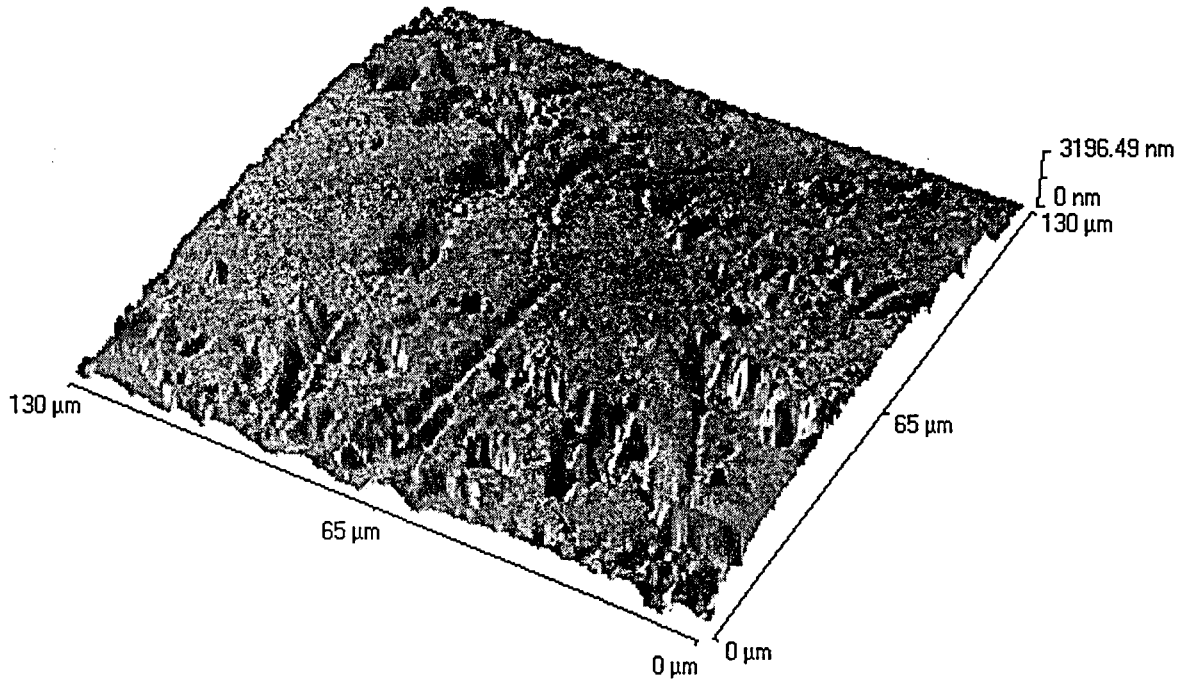
SPM-micrographs 1-4 show the results of the AFM imaging. The images are shown in 3-D mode after shadows were added. Comparing SPM-micrographs 1 and 2, one can clearly see the roughening of the surface of the PVDF capillary membrane during fluorination. By magnifying the image to a 50 μm grid, the much smoother surface of the PVDF membrane, compared with the fluorinated PVDF membrane, can still be seen.

Further work will include:

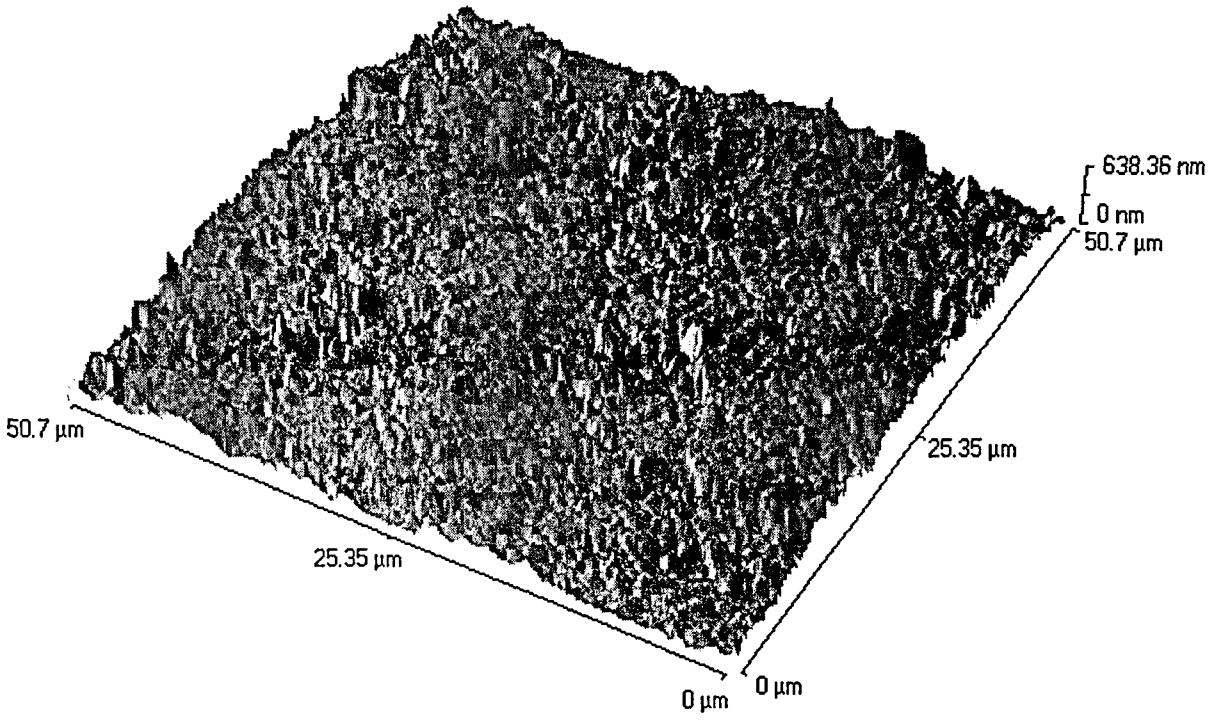
- Measuring the surface roughness induced by fluorination;
- Measuring the depth of the degradation;
- Studying the effect of fluorination conditions on the surface roughening;
- Studying the influence of surface roughness on surface-energy calculations.



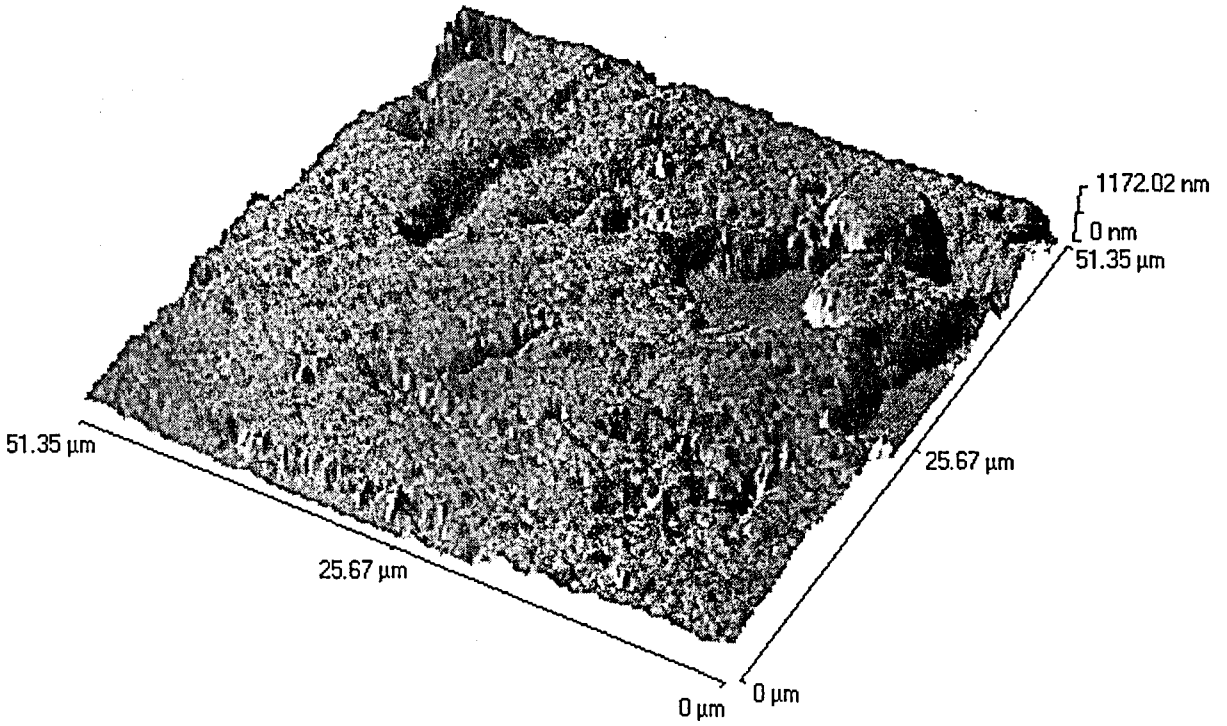
SPM-Micrograph 1: Surface of outside skin of unfluorinated PVDF-capillary membrane at 130 x 130 µm magnification.



SPM-Micrograph 2: Surface of outside skin of fluorinated PVDF-capillary membrane at 130 x 130 µm magnification.



SPM-Micrograph 3: Surface of outside skin of unfluorinated PVDF-capillary membrane at 50 x 50 µm magnification.



SPM-Micrograph 4: Surface of outside skin of fluorinated PVDF-capillary membrane at 50 x 50 µm magnification.

4. OZONATION WITH HOLLOW-FIBRE MEMBRANE CONTACTORS

As mentioned in the introduction, hollow-fibre membrane contactors are highly efficient, in terms of equipment-volume size. The main reason for this is the large area-to-volume ratio (1000 m^2/m^3) in a hollow-fibre membrane contactor. After successful fabrication of a suitable membrane, ozone-to-water mass transfer experiments will be done with the system to determine the mass-transfer coefficient of ozone to water. (This is still to be done, as part of an ongoing project.) Results will be used to compare various cost-effective means of introducing ozone into the water, e.g. bubble-through systems and injectors. The long-term resistance of the membranes to ozone is also to be evaluated.

4.1 Ozone generators

The ozone production capacity of the Ozomatic™ ozone generator (capacity 1 g/h) from Chloromatic **[8]** was tested. This ozone generator is a low-cost system (approximately R7 000 per unit in 1996) which generates ozone by UV-irradiation.

Tests were designed to determine the difference in ozone production when air was substituted for pure oxygen. Flow rates of the gaseous medium were selected with actual applications in mind. Ozone concentrations and production were measured iodometrically **[9]**. From the tables below it is clear that when air was replaced with oxygen, there was a marked effect on ozone production and concentration. When oxygen was used at a low gas-flow rate (0.8 l/min), the concentration of ozone in the medium was 3,7 times greater than when air was used (see Table 2.11). Furthermore, by increasing the gas-flow rate of the medium, the concentration of ozone drops. This was due to the shorter time which the medium spent in the reaction chamber. However, ozone production still increased with flow rate increase, due to the higher throughput of the medium carrying the ozone (see Table 2.12).

Table 2.11: Calculated ozone concentration [O_3] in air or oxygen (O_2) (g/m^3) and ratio

Gas flow rate (l/min)	(O_3) in air ppm	(O_3) in oxygen ppm	(O_3) in O_2: (O_3) in air
0,8	1,933	7,143	3,7
1,8	1,978	5,959	3,0
2,8	1,678	4,719	2,8

Table 2.12: Production of ozone [$g(O_3)/h$] in air or oxygen (O_2)

Gas flow rate (l/min)	[O_3] in air $g(O_3).h^{-1}$	[O_3] in oxygen $g(O_3).h^{-1}$
0,8	0,092	0,341
1,8	0,212	0,640
2,8	0,281	0,789

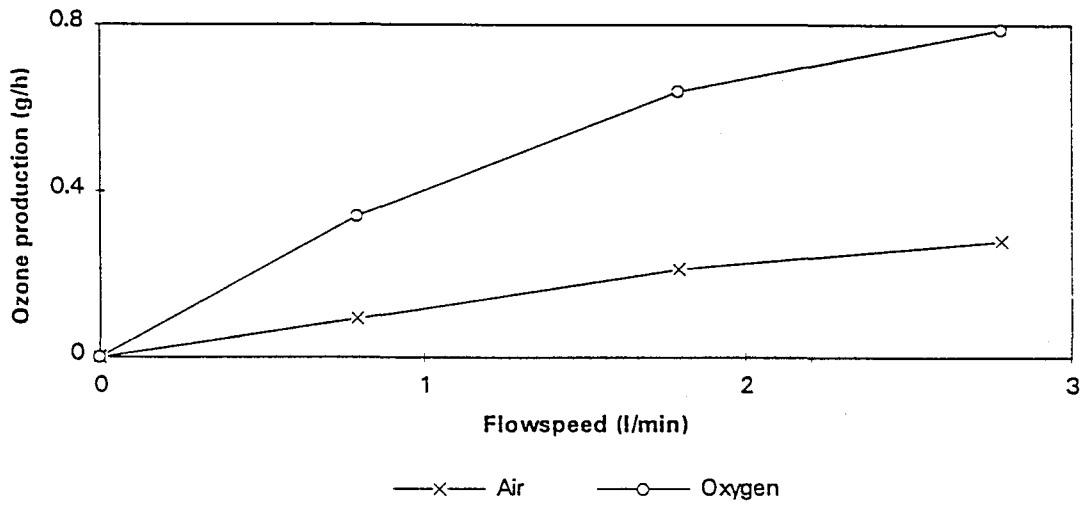


Figure 2.6: Variation in ozone production capacity with flowspeed and feedgas

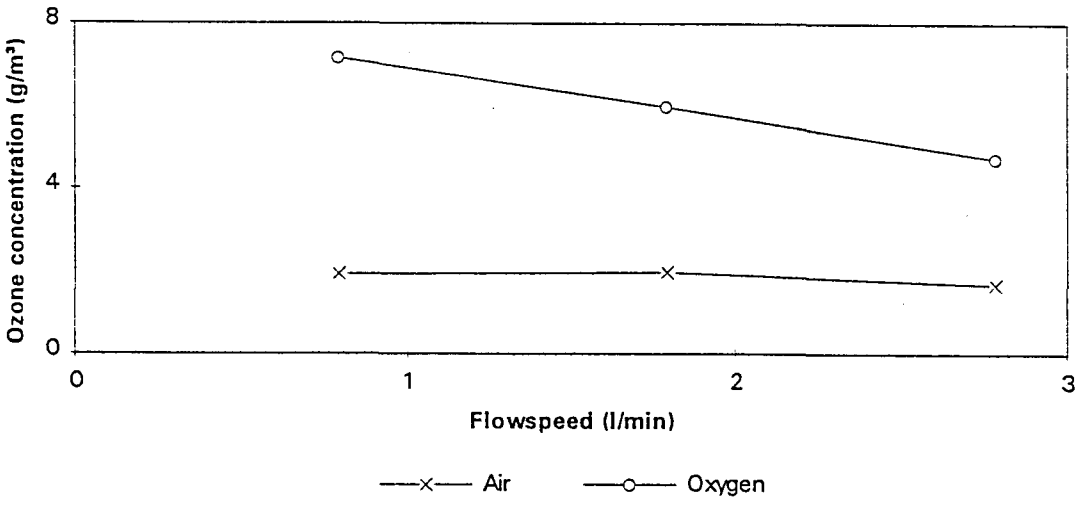


Figure 2.7: Variation in ozone concentration with flowspeed and feedgas

5. PROTEIN ADSORPTION

A number of industrial separation membranes absorb bio-macromolecules such as proteins. This phenomenon is one form of membrane fouling and it reduces permeate fluxes through membranes, and hence adversely affects the economics of membrane separation operations. As mentioned earlier, because of its chemical stability, PVDF has recently come to be considered a good material for membrane manufacture. The further reduction of the surface tension of PVDF has been described. It would be logical, therefore, to conduct tests on protein adsorption to determine the resistance to fouling of both treated and untreated PVDF.

5.1 Experimental: Determination of Protein Adsorption

The abovementioned research was carried out as a joint effort between the IPS and the Department of Biochemistry, University of Stellenbosch.

5.2 Determination of protein adsorption

The fluorinated and unfluorinated PVDF membranes, and control PS membranes, were brought into contact with a 0,1% bovine serum albumin (BSA) aqueous solution at pH 5. After 8 h the membranes were removed from the BSA solution and excess BSA removed by washing with distilled water. The adsorbed proteins on the membranes were removed by washing with a sodium dodecyl sulphate (SDS) solution. The proteins in the SDS solution were then developed by the Folun-Lowry colouring technique and determined by adsorbency measurements at 650 nm[4].

5.3 Results: Protein Adsorption

Some positive results indicated much lower protein (bovine serum albumin) adsorption on fluorinated surfaces than on polysulphone membranes. Figure 2.8 shows the results of this. PVDF (0,99 $\mu g/cm^2$) and fluorinated PVDF (0,94 $\mu g/cm^2$) have a very low protein absorption compared to polysulphone (8.01 $\mu g/cm^2$) in a 0.1% BSA solution. When the concentration BSA in the solution was increased to 1% (by weight) it was found that both the fluorinated and unfluorinated PVDF (2.66 and 2.16 $\mu g/cm^2$, respectively) still adsorb much more of the protein. This may be of significant value in applications of PVDF and other fluorinated surfaces.

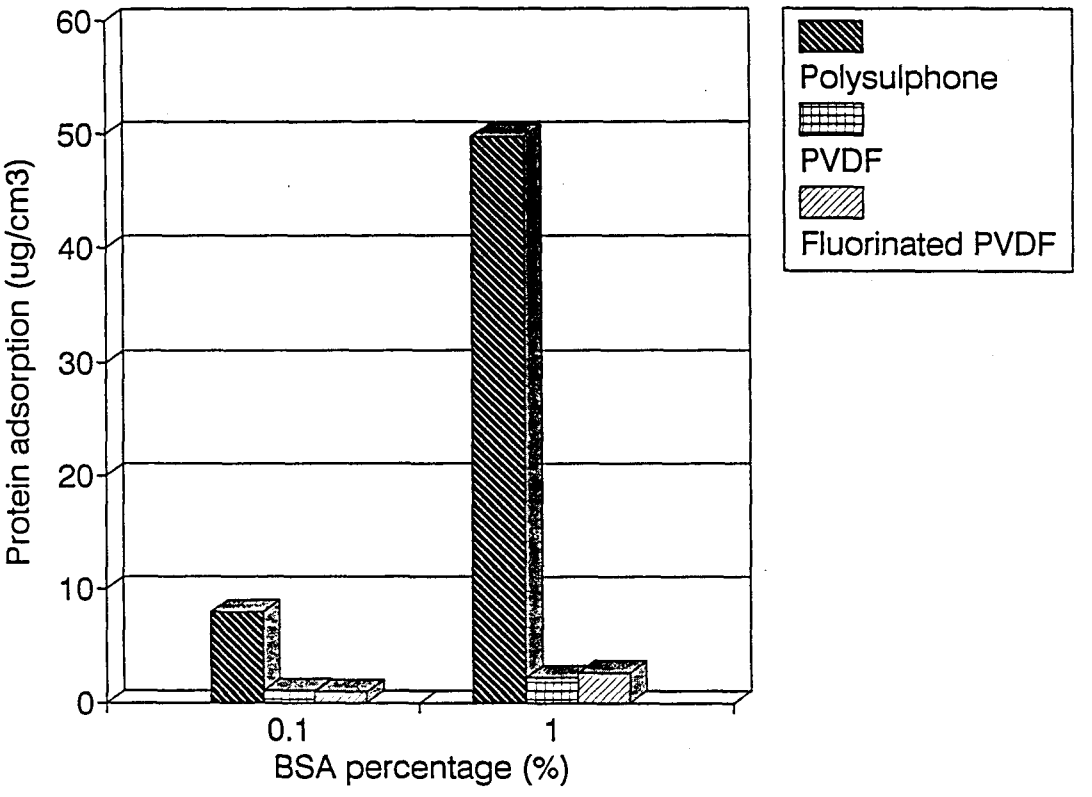


Figure 2.8: Protein adsorption of various membranes incubated for 8 hours in BSA

6. CONCLUSIONS

The overall objective of the project was the creation of gas/water membrane contactors for ozonation of potable and industrial water. This included the following goals:

- The creation of a chemically stable membrane, suitable for ozonation;
- The demonstration of the efficiency of the ozone/water membrane contactor in treating industrial water and providing potable water.

This led to the identification of the following specific objectives for the project:

1. Creation of highly fluorinated PTFE membranes;
2. Creation of highly fluorinated ("Teflon-like") capillary membranes (from 1).
3. Use of the abovementioned membranes in an ozone/water contactor to destroy certain toxic substances in water;
4. Possible study of other applications.

Conclusions are summarized here:

Objective I: Membranes were prepared from PVDF and successfully fluorinated to a higher degree of fluorination. Results of analyses by contact-angle, X-ray photo-electron spectroscopy and solubility, suggest that the degree of fluorination at the surface of this membranes changed, during fluorination, from half-fluorinated to almost fully fluorinated.

Objective II: After a literature study of PVDF capillary membrane manufacture, PVDF capillary membranes with an inside and outside skin, were successfully spun. No polymer additives were used in making this membrane, thus avoiding the limiting effect which such additives may have on the later fluorination of the membrane.

Objective III: The capillary membrane obtained in II was successfully surface fluorinated with fluorine gas and showed the same solubility properties as the surface-fluorinated flatsheet membane did. Atomic Force Microscope micrographs of samples of the fluorinated and unfluorinated PVDF capillary membranes clearly showed the etching of the membrane surface with fluorine, during surface fluorination.

Objective IV: This is the most important objective of the project. The actual study of the mass transfer of ozone to waters of various qualities will commence after finalization of the study of the surface characterization of the PVDF capillary membranes. An aspect of this objective was to obtain an ozone generator of satisfactory properties for rural community water purification. The UV-induced ozone generator has possible applications in the field but, as a research tool, has limited value. This conclusion is based primarily on the lapsed time period experienced for maximum ozone production.

A suitable plant capacity requirement needs to be decided upon before the size of the required generator can be determined.

Objective V: This should become a priority only after objectives I-IV have been reached. The low adsorption of protein onto the fluorinated PVDF membranes shows currently some promise for future work.

7. RECOMMENDATIONS

The research project concerning membrane contactors for ozonation is continuing (1 year extension).

1. Future research should include the characterization of the crystallinity in the membrane structure, pore-size and porosity determination, and optimization of the membrane fabrication procedure to ensure production of a capillary with higher porosity. The latter point will be difficult because a hydrophobic membrane is required for gas/liquid contacting work. This restriction means that no hydrophilic polymer additives can be added to the casting solution during membrane manufacture, which will limit the possible morphologies which could be obtained in PVDF capillary membranes.

2. Further research on the characterization of the fluorinated surface of the membrane should include analyses by XPS, FT-IR, Raman Spectroscopy, Photo-acoustic spectroscopy and Surface energy calculations.

3. Additional areas of study should include an investigation into the possible applications of the fluorinated membranes in other harsh chemical environments. This may include filtration of water containing solvents for unfluorinated PVDF membranes.

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PART 3

MODULARIZATION OF COMPOSITE MEMBRANES

1.1 Introduction

This study formed part of the research project entitled: "Tolerant Membranes", and contributed to the development of reverse osmosis (RO) membrane technology. With funding received from the Water Research Commission and assistance from Membratek (now ENVIG), a study was made of the applicability of local ultra-thin film (UTF) composite membranes developed at the Institute for Polymer Science to standard Membratek module technology.

Two groups of UTF composite reverse osmosis (RO) membranes had been developed at the Institute for Polymer Science (IPS): the poly-2-vinylimidazoline/3-chlorosulphonyl benzoyl chloride (PVAM/SCI) membrane studied by Dr. M.J. Hurndall **[1, 2]**, and described in a final report to the Water Research Commission (1993), and the UTF composite RO membrane, the polyvinylalcohol-piperazine/isophthaloyl dichloride (HOIPS) membrane, researched by Deon Bezuidenhout **[3]**.

Membratek had expressed interest in these membranes, especially for use at the DEBEX plant in Botswana, for the desalination of brackish water to potable standards. Of several types of membranes considered for this purpose, three were selected as being possibly suitable, namely, the membranes designated HOIPS M1X1 (PVAL-based), CAMPIP 3 and CAMOH 5 (PVAM based). Batches of these three membranes, seven tubes per batch, were made up in sufficient quantities to be housed in modules. The tubes were 1,2 m long x 12 mm in diameter.

Tests of the membranes in a single-cell test showed that the membranes complied with Membratek specifications. The membranes were then sent to Membratek to be housed in their modules. Membratek manufactured several modules (2 x HOIPS M1X1; 3 x CAMPIP 3; 3 x CAMOH 5) which were sent to the Institute for testing. The RO test results of the modules compared unfavourably with those for the initial single-cell RO tests **[4]**. Further tests on the original single-cells showed that although the membranes had dried out, they still gave better performances than did those housed in Membratek modules.

Tests of sections of membranes removed from one of the modules showed that the performances met specifications with little or no deterioration. Most of the membranes recovered from the module showed 90%+ rejections. Only a few of the sections showed very low rejections.

1.2 Objectives

A project was therefore undertaken to establish whether IPS UTF composite RO membranes could be housed in Membratek modules. The aim of the project was to build an operational, commerical-size module for housing these membranes.

It was first necessary to determine whether the tubular membranes could be fabricated by IPS in sufficient quantities for scaled-up production, and then to construct a suitable UTF composite membrane RO module, using technology available at the Institute and at Membratek.

It was elected to concentrate on only one type of membrane for the building of a satisfactory module. It was postulated that if an adequate module could be built for one type of composite membrane, then it should be possible to use the other types of composite membrane in similar modules, which should confirm that UTF RO membranes and modules could be manufactured locally. The HOIPS membranes, although showing good experimental RO performance results, were excluded, as the fabrication of these membranes had, at the time, not been mathematically optimised whereas the PVAM/SCI membranes had **[4]**.

Investigations were to proceed with the CAMOH 5 membranes, as all the necessary reagents were either available or could be synthesised from materials in stock.

It was believed that success with this membrane would show that the present module technology in South Africa was adequate for the production of UTF RO modules which would compare favourably with modules made elsewhere and that South Africa might become an independent manufacturer of these modules, without need to rely on technology from abroad.

2. Materials and Methods

2.1 Membrane fabrication

The tubular CAMOH 5 membranes were manufactured according to the process developed at the Institute **[1]**, with relevant changes to the manufacturing process for large-scale production.

The CAMOH 5 UTF RO membranes were manufactured by contacting two components, an aqueous phase and an organic phase, which underwent an interfacial polycondensation reaction. The aqueous phase contained the polymeric precursors of the membrane material, PVAM and PVAL, and the organic phase contained only the monomeric crosslinking agent SCI. The formulation used in making these membranes is given in Table 3.1.

Table 3.1: Formulation for fabrication of CAMOH 5 UTF RO membranes.

Aqueous phase

Component	Quantity (mass %)	Role
PVAM FD	0,96	Barrier material
PVAL	0,24	Hydrophilic agent
TEA	0,20	Acid scavenger
TSP	0,50	Wetting agent
H_2O	98,10	Solvent

Organic phase

Component	Quantity (mass %)	Role
SCI	3,00	Crosslinking agent
Hexane	97,00	Solvent

2.1.1 Reactant solutions

The compositions of the aqueous and organic phases are given in Table 3.1. The methods of making up the solutions are described here. After the required length of the membranes was taken into consideration, glass tubes with an internal volume of just less than 3 ℓ were used in the set-up for batch production. Three litres of each reactant solution were therefore prepared for the production of membranes for a module.

2.1.1.1 Aqueous phase

The components of the aqueous phase are given in Table 3.1. The required amount of distilled water was weighed off and poured into a large Schott bottle. The mass of PVAL needed was then carefully measured, poured into the bottle and a magnetic follower added to the mixture. The bottle was then loosely capped and placed on a heater-stirrer. The mixture was then stirred until the PVAL was in suspension and the temperature had increased to just below boiling. This was done to decrease the time needed for the PVAL to become totally dissolved.

As the PVAL used in the process was of a grade which would have taken days to dissolve completely at room temperature, the solution was heated to shorten the time needed to dissolve the PVAL completely . The solution was then left to cool. The PVAL was added to the water first, as the high temperature needed to dissolve the PVAL would have cured the PVAM, rendering the solution useless for membrane-production purposes.

The other components were then added to the solution, beginning with the PVAM and adding the TSP last, as the addition of TSP resulted in an exothermic reaction at the bottom of the bottle. This allowed resumption of stirring without creating hot spots at the bottom of the bottle. The TEA was added by a drip pipette. The mixture was then stirred until all the components were dissolved in the water and a clear, brownish coloured solution was obtained.

2.1.1.2 Organic phase

The organic phase was simple to prepare. The SCI was usually removed from the freezer in which it was kept (to minimize hydrolysis) and allowed to reach room temperature, at which it is a liquid. The required amount of hexane solvent was measured out into a Schott bottle and a magnetic follower was placed in the bottle. The SCI was then measured directly into the Schott bottle with a drip

pipette. The SCI had to be added quite rapidly, and in a well-ventilated hood. The SCI dissolved readily in the hexane and no heating was required.

2.1.2 Manufacturing process

2.1.2.1 Conditions

The CAMOH 5 membranes had already been optimised, so that the conditions for the fabrication of a specific batch had already been fixed. Tubular ultrafiltration (UF) membranes were used as supports for the CAMOH 5 membranes. The tubular membranes (d = 13 mm) were obtained from Membratek (Pty.) Ltd. (Code: 719) and comprised an asymmetric polyether sulphone (PES) membrane cast by phase inversion onto a polyester support. The membranes were kept in RO water to prevent their drying out. The properties of these membranes are given below in Table 3.2.

Table 3.2: Properties of M719 UF membranes.

Property	Value	Comment
MM Cut-off (dalton)	40 000	5 000 ppm PEG; 0,5 MPa
Fresh water flux (lmh)	400 - 700	0,5 MPa
NaCl retention (%)	< 1%	2 000 ppm NaCl; 0,5 MPa

The supports were removed from the water-bath in which they were kept, allowed to drain in air and then subjected to the precursor dip in which the membrane material was deposited as an aqueous phase on the PES membrane. After removal from the precursor solution they were allowed to air-dry, which left a thin layer of aqueous phase on the PES support. The membranes were then dipped into the organic crosslinking agent solution in which the organic phase formed an interface with the deposited aqueous phase. At this stage the *in situ* interfacial polycondensation reaction took place, to form an insoluble barrier material. After removal of the membrane from the solution, the excess organic phase was allowed to drain in the air. The membranes were then baked in an oven, set at 95°C, to complete the crosslinking reaction in the membrane layer. The membranes were then placed in a water-bath and the water was allowed to run through the tubes to wash away the HCl that had formed during the condensation

reaction, as the presence of the acid species could have reduced the pH resulting in damage to the membranes. The membranes of a batch were then randomly sampled to determine representative RO performance values for the batch, obtained in a single-cell rig. Membranes with adequate RO performances were sent to Membratek for incorporation into modules.

The times of the various steps in the fabrication of the membranes are given in Table 3.3.

Table 3.3: Times of fabrication steps for the CAMOH 5 tubular membranes.

Step	Time (min)
Pre-drain	10
Precursor dip	15
Precursor drain	8
Crosslink dip	6
Crosslink drain	16
Oven bake	5

The above data were used in a spreadsheet program developed at IPS, to generate an optimum manufacturing schedule suitable for mass production of membranes. The output of this program was then formulated into a *Membrane Production Table* (see Appendix) which was used to control the production schedule of the membranes and to be used as a simple quality-control system. By arranging all the different steps in a definite order, it was possible to ensure that no crucial operation was omitted.

Once all the necessary reagents had been prepared **[1]**, it was decided that, since some of them had been stored for quite some time, it was necessary to run a trial to determine whether they were still of adequate quality. For this, small batches (1 ℓ each) of membrane solutions were made up and two pieces of PVC piping

were used to manufacture six CAMOH 5 membranes from the solutions, for testing in the single-cell rig. Table 3.4 shows the components of the solutions.

Table 3.4: Composition of aqueous and organic solutions (vol. 1 ℓ) used in the fabrication of trial CAMOH 5 tubular membranes.

Phase	Component	Amount (g)
Aqueous	H_2O	981,0
	PVAL	2,40
	PVAM	9,60
	TEA	2,01
	TSP	5,00
Organic	Hexane	485,08
	SCI	15,01

The membranes were then tested in a single-cell test rig to determine whether the required performance could be achieved with membranes made with the existing reagents. Retentions of over 85% and some as high as 95% were achieved, which confirmed that existing chemicals could be used.

2.1.2.2 Membrane fabrication set-up

Two glass tubes were made up in a size (d = 60 mm, length = 600 mm) that would just accommodate a tightly packed bundle of 7 supports of the required length. This would allow fabrication of 7 membranes per batch, six of which would be used in the module and one which would be used for quality control in a single-cell test, to determine whether the batch was up to specification.

The glass tubes were placed on a workbench and securely clamped. Several layers of absorbent towelling were placed on the floor against the workbench to absorb all excess liquid that drained from the membranes. The set-up, illustrated

in Figure 3.1, ensured systematic production of membranes. The membranes followed a natural progression from left to right, which minimized the chance of experimental error.

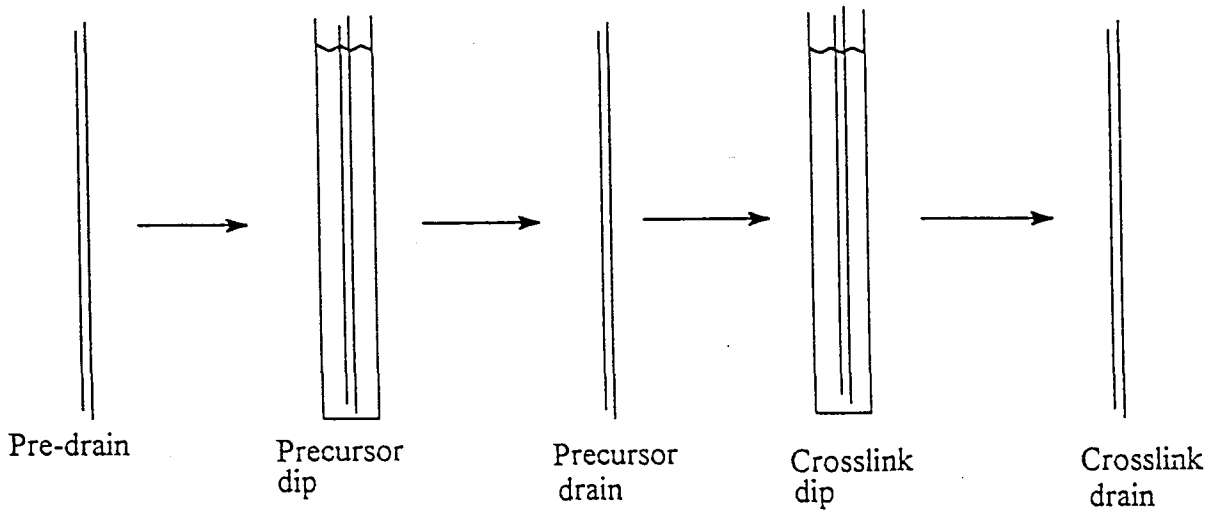

Figure 3.1: Tubular membrane manufacturing scheme.

A specially designed vertical draft oven with automatic temperature control was set to 95°C and allowed to reach this set-point prior to commencing with membrane fabrication. Heat treatment promoted the crosslinking reaction of the PVAM/PVAL film and dried the membranes.

UF supports were removed from the water-bath at the times dictated by the aforementioned production table (see Appendix). The wet supports were then spread out at the pre-drain station, so that the membranes did not touch each other, to allow faster drying. The supports were also wiped on the outside with absorbent cloths to remove the excess water film. This procedure was followed at all the drying stations. The ends of the membranes touching the towelling were also moved to dry places on the towelling, so that the natural wicking action of the towelling would help in removing excess fluid.

In the crosslink step the supports were marked to show to what level the crosslinking agent was in contact with the aqueous film. This was important, so that a piece of membrane from above this mark would not be used in a test or a module, since it would not have a crosslinked insoluble barrier and would be washed away during testing.

Once the membranes were drying at the crosslink drain station, the uncoated ends were pushed through a membrane module spacer and secured with masking tape to prevent the membrane from falling out of the spacer. The batch codes were written on the tape, in order to identify the various batches after fabrication.

A piece of wire with one bent end was inserted into the centre hole of the spacer to allow the membranes to be lowered to the required depth in the oven. The other end of the wire was Y-shaped, with both ends bent so that the ends of the Y could be hooked over the edge of the tube oven, to prevent the membranes from falling into the oven.

After the required drain time, the membranes were baked in the oven and the top ends cut off. The batch code was written directly onto the membrane supports outside, to ensure that it matched the code on the masking tape. The membranes were then placed in a water-bath and well rinsed with water to remove any acid that might have formed during the interfacial polycondensation reaction between PVAM and SCI.

Several production runs were made to fabricate membranes for use in modules. Table 3.5 summarises typical compositions of the aqueous and organic solutions.

Table 3.5: Compostions of solutions for fabrication of four CAMOH 5 module membranes (different production runs)

	Quantities (g) for production run No 1 (2 ℓ)			
Component	1	2	3	4
H_2O	1962,00	1962,21	1962,26	1962,58
PVAM	19,20	19,20	19,202	19,202
PVAL	4,80	4,810	4,813	4,800
TEA	4,00	4,01	4,01	4,012
TSP	10,00	10,000	10,10	10,018
Hexane	1400,00	1400,08	1400,20	1400,02
SCI	43,32	43,34	43,49	43,35
	Quantities (g) for production run No 2 (1 ℓ)			
Component	1	2	3	4
H_2O	-	981,03	981,32	980,45
PVAM	-	9,61	9,612	9,608
PVAL	-	2,400	2,401	2,404
TEA	-	2,01	2,01	2,012
TSP	-	4,999	5,00	5,012
Hexane	-	500,05	500,04	500,14
SCI	-	15,52	15,50	15,70

2.2 Module manufacture

In order to determine whether the IPS UTF composite membranes could be housed in a module, it was decided to first use established module technology, and a module from PCI Membrane System (Britain) was used. Samples of batches of single membranes were tested in a single-cell rig and membranes from a batch with acceptable performance were housed in the module.

2.2.1 PCI module

The PCI module consisted of 18 stainless steel perforated tubes in a stainless steel sleeve, and bolted onto the sleeve were endcaps with machined grooves which connected up the 18 membranes, to form a single continuous tube system.

Membranes with acceptable performance were trimmed to the required length for the module and carefully inserted into the perforated tubes. Rubber grommets inserted into the ends of the membranes formed seals between the membrane and the inner tube of the module.

Care had to be taken to ensure that the grommets were inserted to the required depth to prevent damage to the membranes when the module heads were fitted. Polymeric and metal spacers were placed on both heads to seal them, and the heads were then fitted. Offset pins on the periphery of the head made it impossible to misalign the head with the rest of the module body. The module was then connected to the pump system, and a product tube was fixed to the product outlet so that the module was a closed test system.

2.2.2 Membratek (Envig) modules

Membratek modules consisted of a metal sleeve with a system of spacer rings on the inside that act as supports for the membranes. The ring has space for 19 membranes. These spacer rings were slowly forced over the membranes so that a few rings at a time were forced down the length of the membranes until sufficient spacers had been fitted to support the membrane in the module without any gaps, and the whole assembly was then inserted into the housing sleeve.

The membranes were then connected up into a single system with injection-moulded connectors coated with an adhesive to form a good bond between the membranes and the connector. The two open ends of the module were then epoxy-coated, in a constant-temperature room, with an epoxy that had very little shrinkage, to ensure a tight seal at the module ends. To ensure a good seal the sleeve has concentric grooves in the inside into which epoxy could flow to act as a

plug to prevent leakage past the ends. The epoxy was then allowed to cure and the modules were returned to the Institute for testing.

2.3 Membrane Evaluation

2.3.1 Conditions

All tests on membranes were conducted under similar conditions, irrespective of whether the testing was done on single cells or modules. Table 3.6 gives these conditions.

Table 3.6: Testing conditions for RO membranes.

Parameter	Value
Pressure (MPa)	3,0
Feed solute	NaCl
Solute concentration (mg/ℓ)	2 000
Volumetric flowrate (ℓ/h)	600
Temperature (°C)	20

The volumetric flowrate of 600 ℓ/h is equivalent to a linear velocity in the membrane tube of 1,4 m/s, with turbulent flow. This decreased the thickness of the boundary layer at the surface of the membrane, allowing better diffusion of water to the membrane surface and lowering the effect of concentration polarisation, so that there was a smaller gradient in salt concentration between the bulk concentration and that at the membrane surface. This was due to the transport of water away from the boundary layer, which assists the movement of the dissolved salts away from the membrane surface and back into the bulk fluid.

2.3.2 Test Equipment

2.3.2.1 RO test rig

The equipment used to evaluate the membranes is shown schematically in Figure 3.2. The feed solution was circulated through the membrane test rack by a HYDRACELL D10 diaphragm pump with three chambers, before being returned to the feed tank. The volumetric flowrate was measured on the rotameter, while the pressures at the inlet and outlet were measured by pressure gauges P1 and P2, respectively. A bypass in the piping system allowed the operator to control the flowrate and pressure in the test sections by the manipulation of the control valves V1 and V2. The feed solution was kept at a constant temperature by means of cold water (4°C) from a cold-water tank flowing through the cooling coil.

The temperature of the feed solution was measured by a thermocouple in the feed tank, and fed to a temperature controller (TC) which controlled a solenoid valve, V3. The test rack consisted of five test cells connected in series. The cells consisted of a perforated metal tube which acted as the support for the membranes in a plastic housing. The permeate from each 500-mm-long cell was returned to the feed tank in order to keep the solute concentration of the bulk fluid constant. The membranes were inserted into the metal pressure housing and cut to the correct length.

The ends of the membrane were sealed by a rubber grommet inserted into the membrane. Care had to be taken to ensure that the grommet fitted perfectly, otherwise the ends of the cell would leak bulk fluid into the permeate flow, lowering the measured retentions.

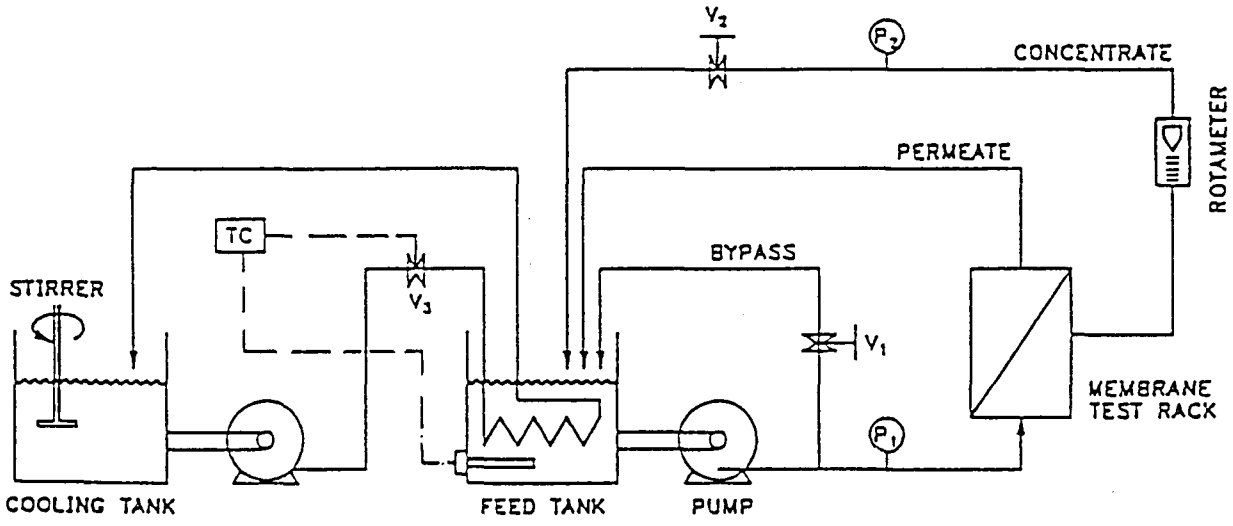

Figure 3.2: RO testing rig.

The modules were tested on the same test rig as that used for the single-cells as pictured in Figure 3.2. Modules were tested by uncoupling the test rack from the system and fitting the module into the test rig. The permeate was also returned into the feed tank.

2.3.2.2 Conductivity measurement

Conductivity was measured in a cell connected to a RADIOMETER COPENHAGEN CDM 83 conductivity meter. Water from a constant-temperature bath (30°C) was circulated through the cell. The cell was calibrated daily with a 2 000 mg/ℓ NaCl solution.

2.3.3 Experimental procedures

The feed tank was filled with a known volume of RO water to which NaCl was added. The feedtank was then adjusted to the required NaCl concentration (2 000 mg/ℓ) by circulating the solution through the system and adding concentrated salt solution or water, as needed. The concentration was indirectly measured using a conductivity meter. The pressure and flowrate were then adjusted to the required values and the system allowed to run for some time to allow it to reach a steady-state, before any measurements were made. If there was any need to restart the system, the same procedure was followed. The product production rate was measured with a volumetric flask and a stopwatch. The conductivities of the permeate and the feed solution were used to determine the flux and retention rates of the membranes being tested.

The relationship between conductivity and concentration was assumed to be linear at the levels at which tests were carried out. The concentrations in the equation for determining retention could therefore be replaced by the conductivities of the permeate and feed without any appreciable error. The NaCl retention of a membrane was determined by using equation 3.1:

$$\text{Retention} = \left(1 - \frac{\text{permeate conductivity}}{\text{feed conductivity}}\right) \times 100\ \% \qquad (3.1)$$

Water production rates (flux) were calculated by the equation:

$$F = \ell mh\ (\text{Litre/m}^2.\text{h}) \qquad (3.2)$$

If this equation was normalized and the area of the membrane was taken into consideration, this equation could be written as follows:

$$\frac{{}^{1}\!/_{1000}}{\left[{}^{a}\!/_{10000000}\right]\left[{}^{t}\!/_{3600}\right]} \qquad (3.3)$$

where v is volume (mℓ)
a is surface area (mm^2)
t is time (s)

The permeate flowrates were therefore converted to fluxes by incorporating the available surface area of the membrane:

$$Flux_{sc} = \text{Flowrate } (m\ell/s) \times 273,4 \quad (3.4)$$

where 273,4 is a factor to allow for conversion of units

The modules were tested and permeate collected in a 2 ℓ volumetric flask; this constant was therefore combined with the equation for calculating the flux (3.3), so that a factor X flowrate was not necessary to determine the flux, but the two were combined so that the time taken to fill the 2 ℓ flask was used directly to find the fluxes.

Membratek module: $Flux_{Mem} = 7\ 720,4/t \quad (3.5)$

PCI module: $Flux_{PCI} = 8\ 491,7/t \quad (3.6)$

where t = the time taken to fill the 2 ℓ volumetric flask.

Similarly, if in single-cell tests the volume measured was always 50 ml, flux was calculated by:

Single-cell: $Flux_{SC} = 9\ 094,6/t \quad (3.7)$

where t = the time taken to fill the 50 mℓ volumetric flask.

2.3.4 Membrane manufacture, modularisation and testing

Two sets of CAMOH 5 membranes were made up as described in Sections 2.1.1 and 2.1.2.1 and tested in a single-cell rig to determine whether they were of suitable quality. Tests were successful, indicating that several batches of membranes could be manufactured from the same solutions without any deterioration in retention properties. The membranes exhibited good performances, ranging from 93% to 98,9% retention on , when tested at 20°C, 600 ℓ/h flow rate and 3.0 MPa applied pressure. These results led to the decision to use the rest of the membrane batch in a PCI module to determine how the CAMOH 5 membranes would respond to being modularised in an established system.

Membranes from the abovementioned batch, used to check the manufacturing process, were inserted into the PCI module. The module was connected to the same pumping system as used for the single cells. The pressure in the module was then slowly raised, over a period of 3 h, to 3.0 MPa and the membranes were

evaluated. Retentions of above 98% were observed. A further batch of CAMOH 5 membranes was therefore made for modularisation in Membratek modules. The single-test membranes exhibited adequate performances and the membranes were then sent to Membratek to be housed in modules.

The successfully operating PCI module was replaced with the Membratek module. The test results of this first attempt at modularising the membranes in a Membratek module were most disappointing as there was a significant drop in retentions. The module was then scrapped and another batch of membranes prepared. A second module was made up by Membratek but, on return of the module it was found that, due to a heatwave in Paarl, the room in which the heads of the module, are epoxied had not been kept at the correct temperature, which resulted in the epoxy shrinking, causing damage to the membranes and leakage past the heads.

It was found that during building of the modules at Membratek the UTF membranes were rather roughly handled, which was considered to be unacceptable for this type of membrane. The UTF composite RO membranes resembled, in appearance, the robust UF membranes which are used as support for the CAMOH 5 membranes, and the assembly staff are, to date, familiar only with working with membranes which can tolerate rough handling. It was therefore decided that IPS staff would oversee the building of module No 3 (the fourth module in the test) at Membratek to ensure that sufficient care was taken in the manufacture of the module. It was also found that the original rings used in the construction of Membratek modules fitted very tightly onto the membranes and that they were required to be forced onto the membranes. A new set of rings was made and these fitted much better. These were then used for the CAMOH 5 module and proved to be a success.

This module was tested for some time, but a long-term test was interrupted when a cooling system on the rig broke down over a weekend, which resulted in very high temperatures in the system and failure of the membranes. Regeneration of the membranes was attempted, using a method developed by Morkel **[5]**, but this was unsuccessful.

It was assumed that the adhesive-coated elbows used to connect the membrane tubes in series could have been the cause of the failure. The temperature cycling to which the module had been subjected probably created mechanical stresses in the adhesive joint, leading to either outright module failure or fatigue failure of the adhesive joint. This would have led to leakage of the bulk fluid into the permeate side, with the resultant loss in retention and a large increase in flux. Membrane regeneration materials would not have improved performance.

3. Results and Discussion

The results obtained from all the tests used to evaluate the membranes and modules are presented. Four production runs were made to manufacture membranes for incorporation into modules. A membrane from each batch, randomly sampled as representative of the whole batch, was used in single-cell tests to determine whether the membranes of that batch were suitable for use. Results of single-cell tests of each production run determined which membranes would be used in the manufacture of modules and which would be rejected. Only the membranes that gave the highest retentions would be used for incorporation into modules, that is, the batch with the highest retentions would be used preferentially, then the batch with the next best retentions and so on.

The first production run was made to test the materials to be used in the production of the membranes. The same solutions were re-used to determine when the solutions become spent, which would have resulted in membranes not suitable as RO membranes. In the remaining three production runs further single-cell tests were done to select batches for module fabrication.

3.1 First production run

This experiment was intended to show at what point the solutions used for membrane preparation would become spent and to select the best membranes, with regard to retentions, for incorporation into modules.

The first batches made in the first production run gave mixed results. It was expected that the retentions would slowly deteriorate as more membranes were made from the same solutions. No trend in decline of performance was, however, discernible. It is possible that the expected decline in retentions will become more obvious as yet more batches are made from the same solutions. A method that could be investigated to quantify when a solution will be spent, is to determine what area of membrane could be produced from a given solution volume before membrane properties became unacceptable.

The retentions of CAMOH 5 membranes in a single-cell test increased slightly in the early stages of membrane life to a practically constant value (average of 5 membranes was 98,5% retention after 80 hours of testing). The retention and flux performances of individual batches fabricated for incorporation into a PCI module are shown in Figure 3.3.

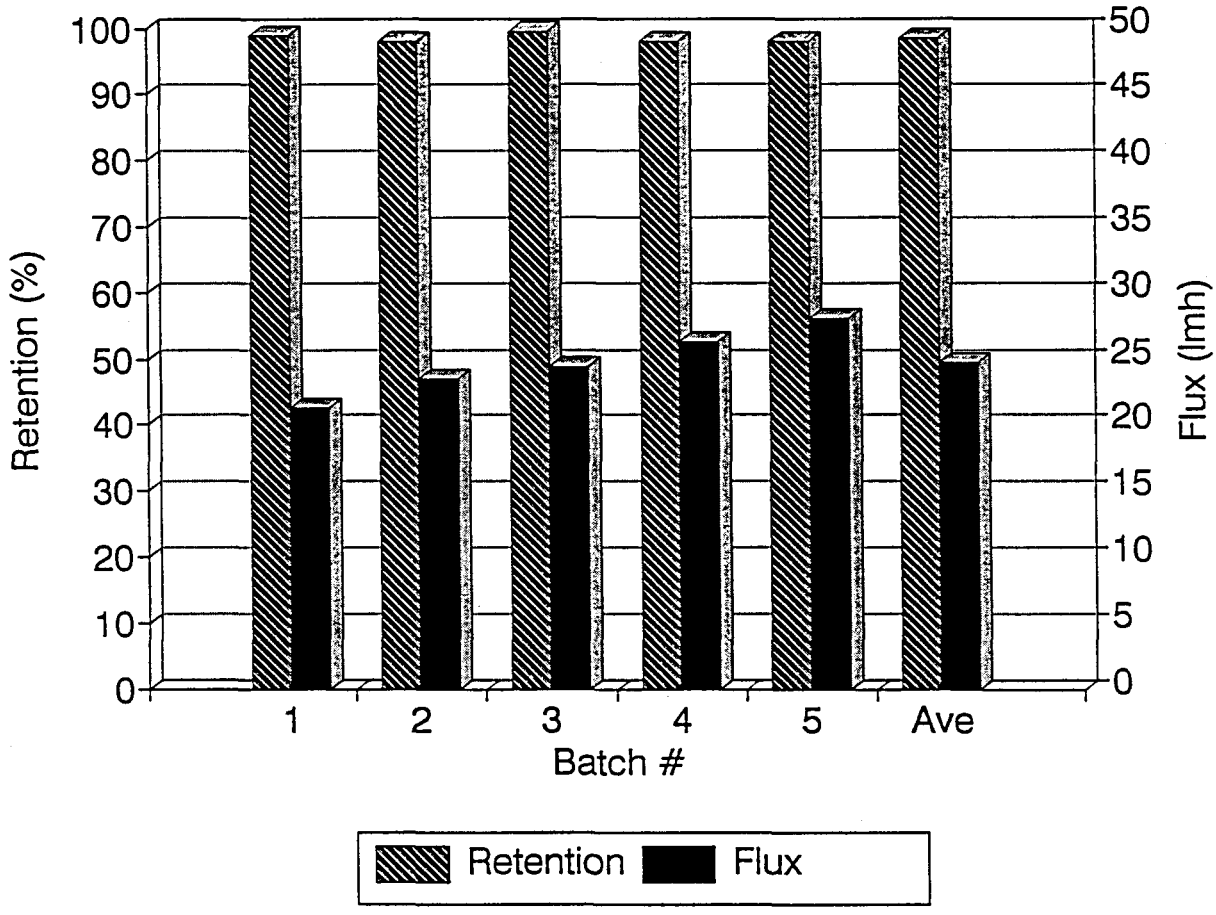

Figure 3.3: Retention and flux of CAMOH 5 membranes (production batch for PCI module)

3.2 PCI module

Figure 3.4 shows the expected retention, based on single-cell data of a module made from the first production run, to be 97,2% and the flux to be 21,8 ℓmh. The results of the CAMOH 5 membranes housed in the PCI module were, in fact, above the values that were expected from the single-cell results. The average retention was up to 98,6%, while the flux was also much higher than expected, at 42,4 lmh. These results are also illustrated in Figure 3.4, which shows retentions and fluxes for the first four measurements, with the predicted result.

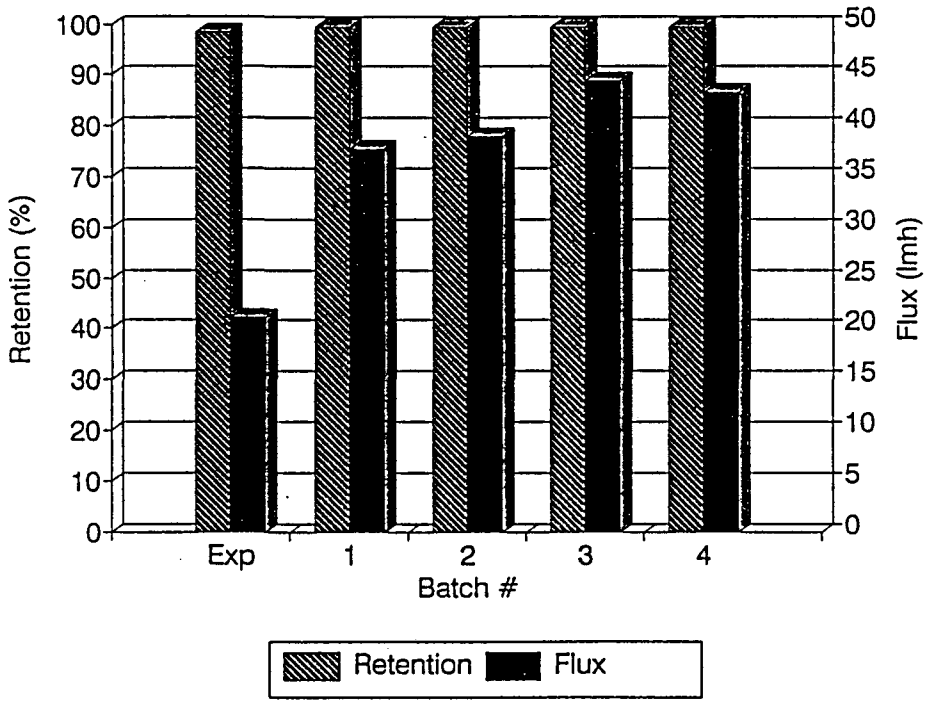

Figure 3.4: Retention and flux of CAMOH 05/PCI module. Module performance v/s expected performance

3.2.1 Long-term results

To gather long-term data, the PCI module was run for more than 900 h. There was no decline in the retention of the module, it remained practically constant at 98,8% retention. There was, however, a slow decrease in flux from a high of 44,2 lmh (a decrease of about 7%). This was expected of a membrane run for some time without any cleaning. The 900 h represent more than a month of continuous use. Test results are illustrated in Figure 3.5.

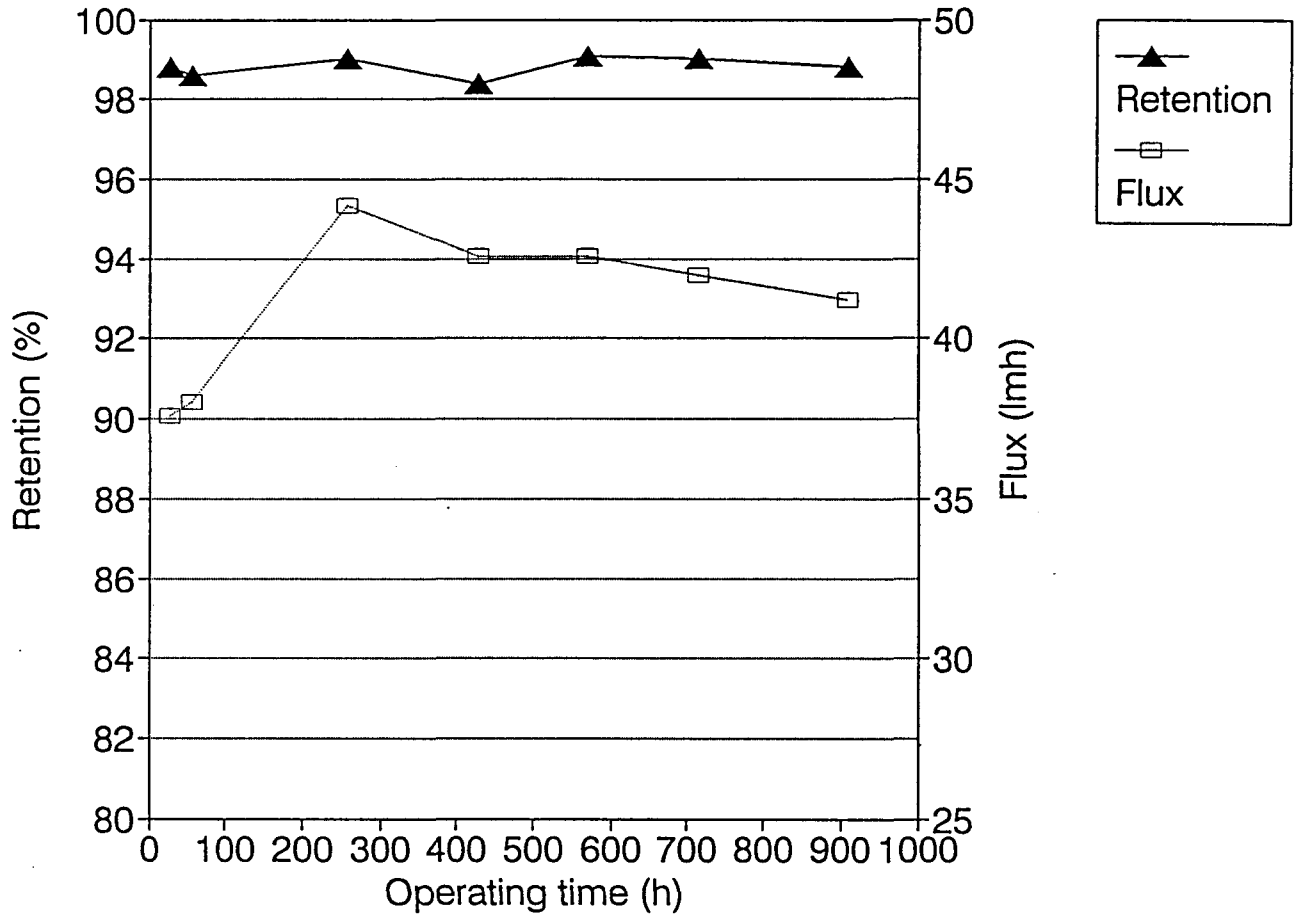

Figure 3.5: Long term text: CAMOH 5 membranes in PCI module

3.3 Membratek module No 1

This module had very low retentions, less than 60%, compared with the single-cell test results of more than 85%. The module also had a very high flux, much higher than that of the single cell, leading to the belief that the membranes had either been damaged during insertion into the module, or that the membranes had been stored incorrectly or for too long, prior to modularization.

3.4 Membratek module No 2

The single-cell tests once again showed very good results, and the membranes were sent to Membratek for incorporation into modules. The module could not, however, be tested as both the ends of the module began to leak as soon as

pressure was applied to the module. This was due to shrinkage of the epoxy used to seal the ends of the metal sleeve.

3.5 Membratek module No 3

The third Membratek module was a success.

This module showed excellent RO performance results; retentions were well above 90%. This module was therefore the first successful locally produced UTF RO module. This module showed that South Africa did have the know-how and the skills to produce UTF composite tubular membrane modules and would not have to rely an overseas technology for these type of membranes.

Figure 3.6 shows the results of the single-cell test done on the fourth production run and the expected retention of a module fabricated from these membranes. It also illustrates the retentions and fluxes of the different batches made in the production run.

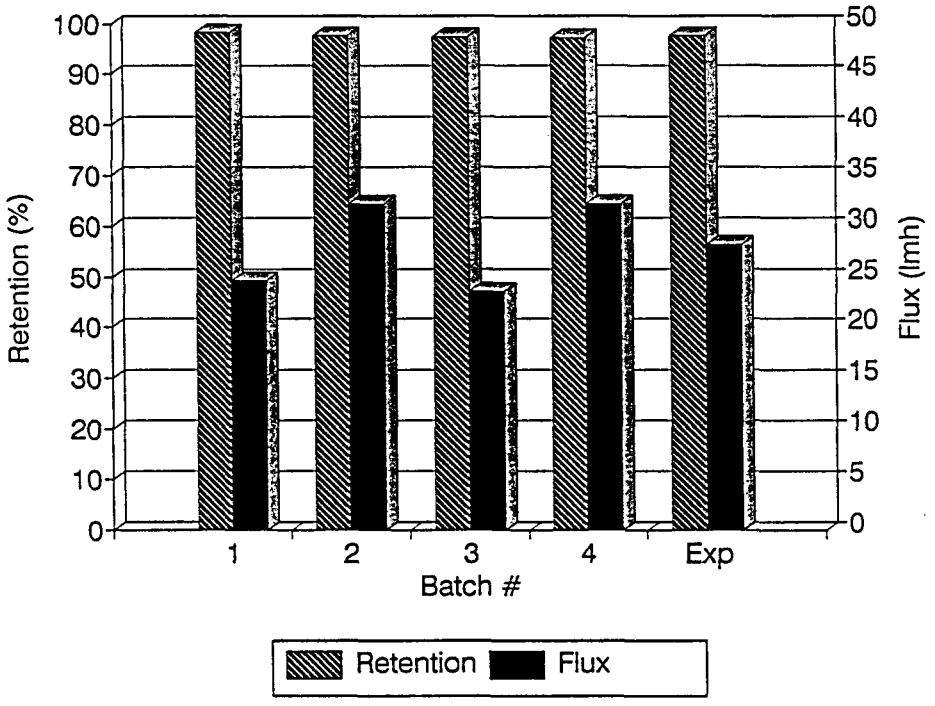

Figure 3.6: Retention and flux of CAMOH 05 (production batch for Membratek module No 3)

Figure 3.7 illustrates the expected results for the module and the actual results achieved. As can be seen, the expected and achieved retentions were very close (97,7 vs. 98,0%), but the module delivered a higher flux than expected (27,6 vs. 33,9 ℓmh), that is about 22% higher. These improvements were also observed in the PCI module evaluations.

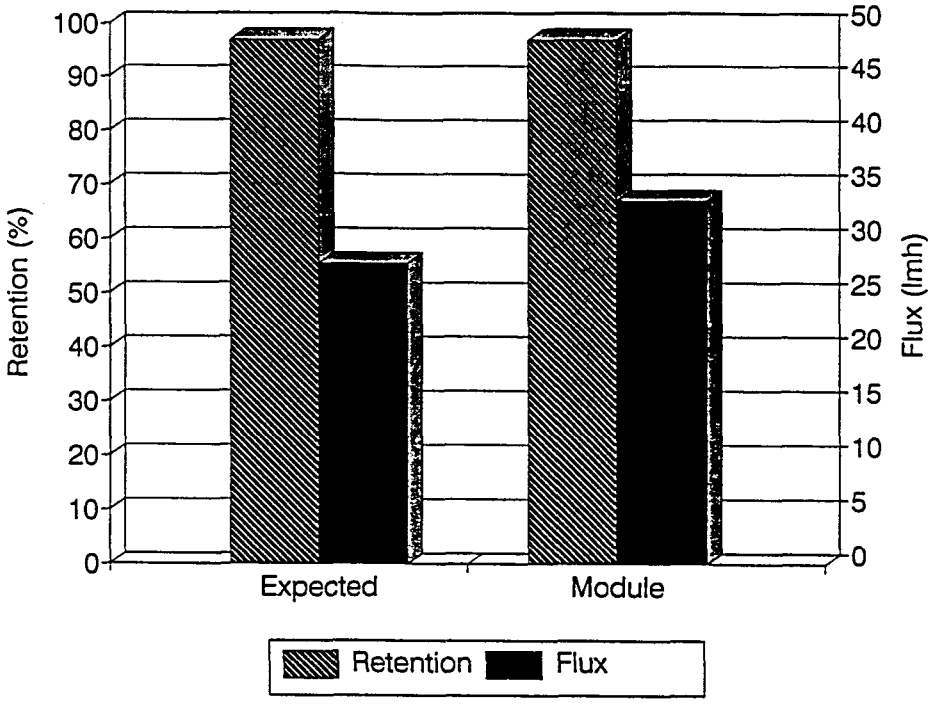

Figure 3.7: Retention and flux of CAMOH 05 membranes (results of Membratek module No 3)

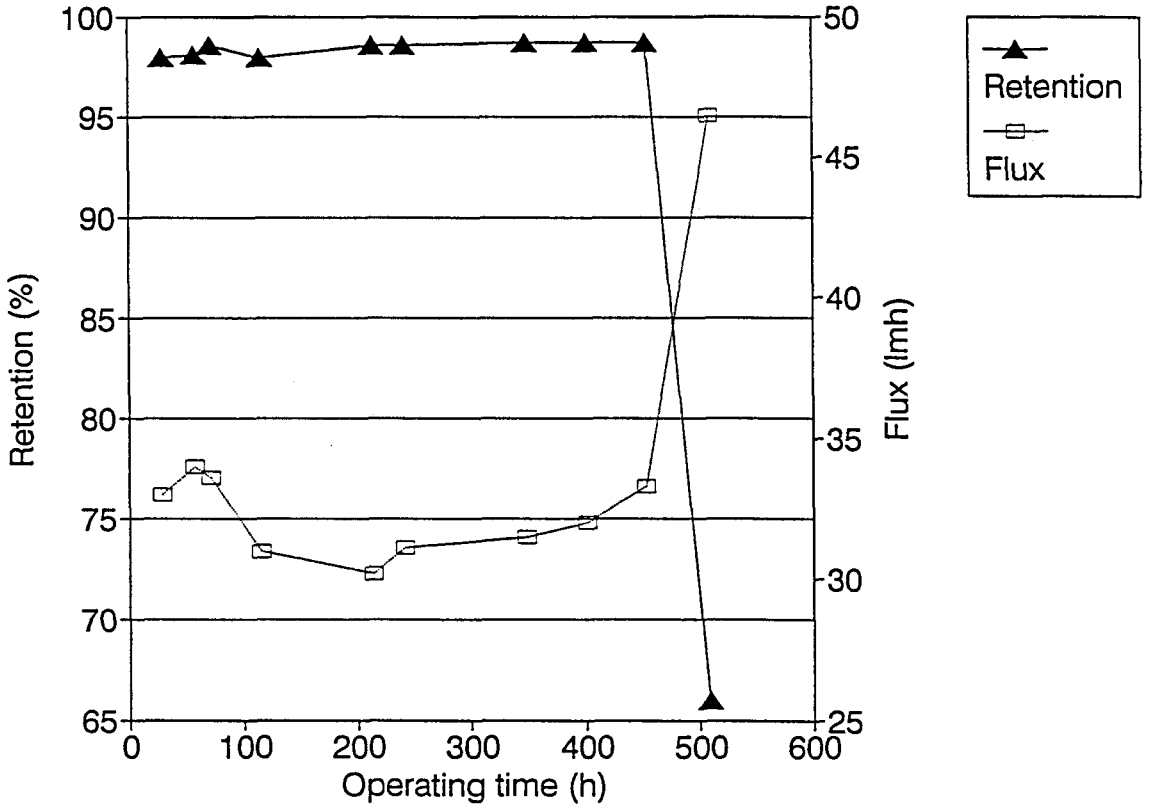

Figure 3.8: Retention and flux of CAMOH 05 membranes in a Membratek module v/s test time

The module was then run for more than 500 h during which time the retention was high, above 98%, and it remained practically constant, until 414 h. There was however a marked decline in retention during the period between about 450 h and 509 h. This was due to the failure of the large cold-water circulating pump caused by blown solenoids. Because of the lack of available cooling water (4°C) and the continued high-pressure operation at 3,0 MPa, the temperature of the system rose. (This happened during a hot weekend and, when the fault was discovered, the module was found to be running at well above 45°C.) This resulted in permanent damage to the module, rendering it useless for RO.

The fact remained nonetheless, that the module was the first successful, locally produced UTF composite RO module.

3.6 Regeneration

The failed module presented a good opportunity to test a membrane regeneration technique developed at the Institute **[5]**. The regeneration material was a resorcinol-formaldehyde resin with chemically reactive sites. A solution of the resorcinol-formaldehyde resin was added to the feedwater in the required concentration, based on the volume of water circulating in the system. The feedwater tank and system had a total volume of about 37 ℓ. The resin solution (12,40 g, equivalent to 1,85 g resin) was added to the feedwater and the temperature was raised to 40°C for 3 h to allow the resin time in which to react with the membrane material. The resin was used in an attempt to reverse the degeneration of the membrane, but as can be seen from Figure 3.9 this was unsuccessful.

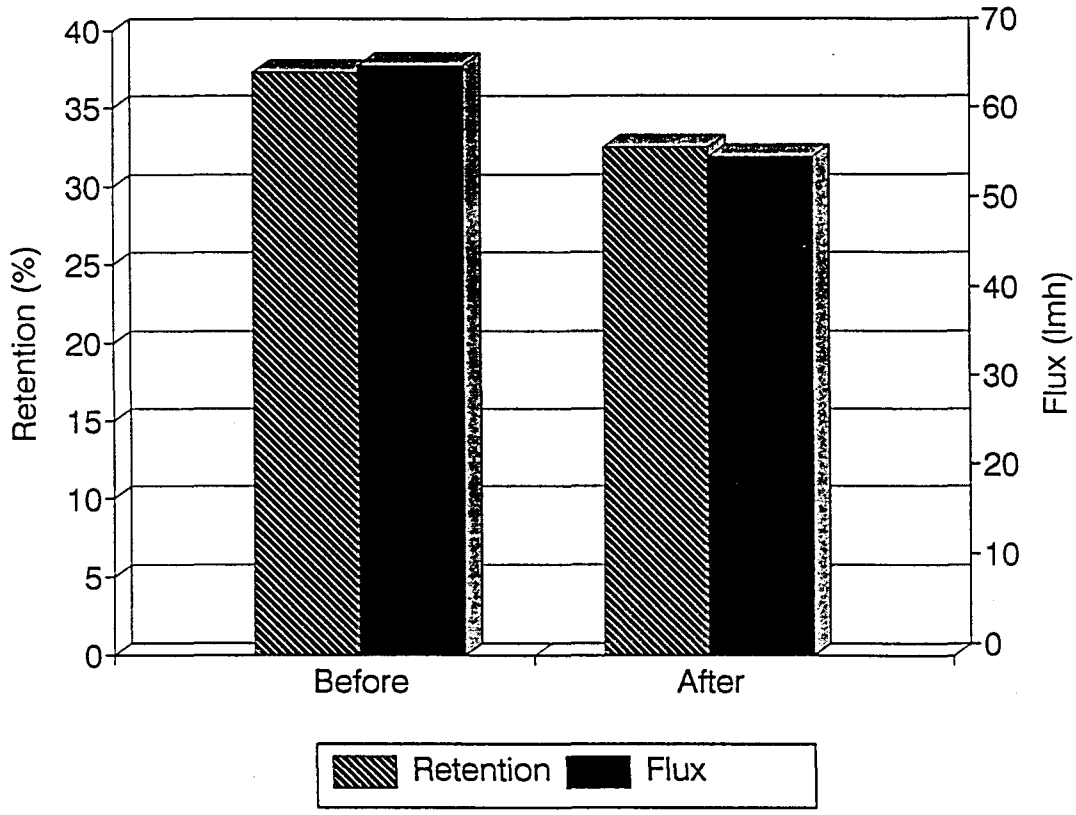

Figure 3.9: Test results of a CAMOH 05 module before and after regeneration with a resorcinol-formaldehyde resin

4. Conclusions and Recommendations

4.1 Conclusions

An IPS UTF composite RO membrane (CAMOH 5) could be modularised in a local Membratek module, that gave performances comparable with those obtained by similar membranes in the well known module of PCI Membrane Systems (Britain).

4.2 Recommendations for future consideration and technical transfer

It has been demonstrated that UTF composite membranes developed at the Institute could be modularised with Membratek technology. There is, however,

room for improvement, both in manufacture and in the technology used. The most important factors that still require attention are:

1. Research should be conducted into the best way to mass-produce the membranes in the shortest time possible. Possible avenues to investigate include: ways of reducing human handling of the membranes, that is, automating the manufacturing of the UTF membranes; the effect of air-blowing the tubes after the dip-coating process to shorten the drying time needed in order to reduce the time needed to manufacture a batch; electronic measuring and dosing of concentrated membrane materials into the solvent to keep the concentrations of these materials at their required levels as this would be more cost effective and allow longer production runs before a new batch of solution is required. This would increase the number of membrane batches or number of membranes that could be made using a single batch of solution, before there is any deterioration in membrane properties.

2. The storage characteristics of the membranes should be accurately determined. The longer the membranes can be stored without any deterioration in properties, the earlier the manufacturer can start with membrane production. This would significantly reduce any manufacturing bottlenecks that might result from a big contract that must be completed in a short time.

3. The economics of storage life of membranes vs. production capacity of the membrane plant (number of membranes per time unit) should be optimised. Plant and equipment cost will be set by the production capacity and operating costs for different schemes, that is, the number of tubes per batch, the volume of solution, how often solution must be replaced, etc. The production capacity would be influenced by the likely size and timescale of any received order. This could best be decided upon by people who work in the industry and have a knowledge of membrane manufacture on a large scale. They should have the necessary expertise to enable them to decide on any possible situation which might develop, should local production of UTF RO membranes be required.

4. Research should be conducted into new ways of manufacturing modules, so that an effective system could be developed that would decrease the risk of damage to the composite membranes during installation of membranes into the inner support structure (the present ring system). A probable avenue to explore would be to manufacture an inner support structure in which the membranes can be laid onto the support and the next layer of the support laid

over the membranes. This would limit the possibility of damage to the UTF membranes as it would not be necessary to force the membranes into the support structure, which leads to a membrane being bent, and cracking of the thin polyamide barrier layer. The support would have to have the structural strength to support the membrane at pressures of up to 5 Mpa. It would also have to be porous to allow permeate to flow to the permeate outlet of the module. A process that might be considered is the formation of porous plastic parts from powder, using microwaves to heat the powder in a mould. (This is being done by a British company and it is said to be less expensive than sinterforming.)

5. Tests should be done on the failed module (the third Membratek module) to determine whether the failure was caused by failure of the adhesive or related problems of the connecting elbows, or by some other cause.

6. If the modules are to be produced commercially, workers at Membratek should be trained as a special group working on the UTF membranes. They should be made aware of the need for careful handling of the UTF membranes which are more fragile than the asymmetric CA and PS membranes.

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Membrane Production Table

Predrain Time (min):	10	Date:	...../...../.....
Precursor Wet Time (min):	15	Experiment #:	.....
Precursor Drain Time (min):	08	Substrate:	.....
Crosslink Wet Time (min):	06	Precursor:	.....
Crosslink Drain Time (min):	16	Crosslinker:	.....
Oven Drying Time (min):	05	Oven Temp:	.....
Total Time (min):	60		
Time between Batches (min):	17		

00	Drip dry [1]	1' 18	Prec in	2' 16	Drip dry [9]	3' 12	Xlink drain
10	Prec in	1' 24	Xlink in	2' 20	Oven in	3' 15	Prec drain
17	Drip dry [2]	1' 25	Drip dry [6]	2' 21	Xlink drain	3' 16	Oven out [9]
25	Prec drain	1' 29	Oven in	2' 24	Prec drain	3' 17	Prec in
27	Prec in	1' 30	Xlink drain	2' 25	Oven out [6]	3' 23	Xlink in
33	Xlink in	1' 33	Prec drain	2' 26	Prec in	3' 24	Drip dry [13]
34	Drip dry [3]	1' 34	Oven out [3]	2' 32	Xlink in	3' 28	Oven in
39	Xlink dry	1' 35	Prec in	2' 33	Drip dry [10]	3' 29	Xlink drain
42	Prec drain	1' 41	Xlink in	2' 37	Oven in	3' 32	Prec drain
44	Prec in	1' 42	Drip dry [7]	2' 38	Xlink drain	3' 33	Oven out [10]
50	Xlink in	1' 46	Oven in	2' 41	Prec drain	3' 34	Prec in
51	Drip dry [4]	1' 47	Xlink drain	2' 42	Oven out [7]	3' 40	Xlink in
55	Oven in	1' 50	Prec drain	2' 43	Prec in	3' 45	Oven in
56	Xlink drain	1' 51	Oven out [4]	2' 49	Xlink in	3' 46	Xlink drain
59	Prec drain	1' 52	Prec in	2' 50	Drip dry [11]	3' 49	Prec drain
60	Oven out [1]	1' 58	Xlink in	2' 54	Oven in	3' 50	Oven out [11]
1' 01	Prec in	1' 59	Drip dry [8]	2' 55	Xlink drain	3' 57	Xlink in
1' 07	Xlink in	2' 03	Oven in	2' 58	Prec drain	4' 02	Oven in
1' 08	Drip dry [5]	2' 04	Xlink drain	2' 59	Oven out [8]	4' 03	Xlink drain
1' 12	Oven in	2' 07	Prec drain	3' 00	Prec in	4' 07	Oven out [12]
1' 13	Xlink drain	2' 08	Oven out [5]	3' 06	Xlink in	4' 19	Oven in
1' 16	Prec drain	2' 09	Prec in	3' 07	Drip dry [12]	4' 24	Oven out [13]
1' 17	Oven out [2]	2' 15	Xlink in	3' 11	Oven in		

INSTITUTE FOR POLYMER SCIENCE
WRC FUNDED RESEARCH OUTPUTS: 1994-1996
PROJECT: TOLERANT MEMBRANES

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1994

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2. CHAPTERS IN BOOKS

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5. DEGREES COMPLETED

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2. **D.G. Bessarabov.** PhD. December 1996.

3. **C.E. Morkel.** MSc. December 1996.