DEVELOPMENT OF TOLERANT MEMBRANES

by

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LIST OF ABBREVIATIONS

CA	Cellulose acetate
Cl_2S	3,5 Dichlorosulphonylbenzoylchloride
DAB	Diaminobenzene
DETA	Diethylenetriamine
EDA	Ethylenediamine
IPC	Isophthaloyl dichloride
$K_2S_2O_8$	Potassium persulphate
lmd	Litres per square metre per day
MVE-*alt*-MAH	poly(methyl vinyl ether-*alt*-maleic anhydride)
NaOCl	Sodiumhypochlorite
NF	Nanofiltration
PDAA	Polydiallylamine
PEI	Polyethyleneimine
PES	Polyethersulphone
PIP	Piperazine
PVAc	Polyvinylacetate
PVACVAPE	Polyvinylalcohol-co-vinyl p-amino phenylether
PVAL	Polyvinylalcohol
RO	Reverse Osmosis
TEA	Triethylamine
TMC	Trimesoylchloride
UF	Ultrafiltration
UTF	Ultra thin film

Types of Membranes

PK	Gel layers of PVAL + $K_2S_2O_8$
PKPA	Membrane prepared by deposition of PIP/IPC desalting barrier on top of PK gel layer
PPIP	Membrane formed by precursor of PIP + PVAL crosslinked with IPC or TMC
PPDAA	Membrane formed by PIP + PDAA, crosslinked with IPC
CAMOH	Membranes prepared from precursor of PVI + PVAL, crosslinked with SCI
CAMPIP	Membranes prepared from precursor of PVI + Piperazine, crosslinked with SCI
PVI	Poly-2-vinylimidazoline
PVI-CFD	Poly-2-vinylimidazoline, with reduced EDA content
PVI-FD	Poly-2-vinylimidazoline, isolated by freeze-drying
PVI-OD	Poly-2-vinylimidazoline, isolated by oven-drying

EXECUTIVE SUMMARY

BACKGROUND AND MOTIVATION

The availability of adequate quantities of quality water is of vital importance to South Africa and this need is ever increasing. Membrane processes can make a most valuable contribution to restore or improve the quality of water resources and aqueous effluent streams, as they offer a viable technology for the re-use of water. Since the inception of the polymeric semi-permeable membrane, demands on and requirements for reverse osmosis (RO), ultrafiltration (UF) and later, nanofiltration (NF) membranes developed fast. These membranes differ both in the materials and methods of fabrication and their ability to filter different constituents of aqueous streams; they are useful in many varied applications. At present only tubular CA RO membranes and a series of tubular PES UF membranes are available locally. It became necessary to develop newer membrane systems which could fulfil the requirements of the market.

It was proposed that research be conducted into the creation of a new family of low-pressure membranes, operating below 2000 kPa.

OBJECTIVES

The main objective of this contract was to generate a family of low-pressure thin-film membranes, useful for water desalination. Two classes of membranes were to be considered:

(a) a medium to high NaCl-retention reverse osmosis (RO) membrane, exhibiting 85 - 95% retention at operating pressures of 1 500 - 2 000 kPa, and

(b) a low to medium NaCl-retention nanofiltration (NF) membrane, exhibiting 40 - 60% retention at operating pressures of 500 - 1 000 kPa.

These membranes were to be made after carefully studying the chemistry of various polymeric materials and with consideration for the many variables which pertain to the making of synthetic membranes.

The following types of thin film synthetic membranes were selected for investigation and the following studies were conducted:

1. Polyvinylalcohol (PVAL) membranes:

(i) Evaluate different techniques and reagents to produce insoluble PVAL films; Test films for RO and/or NF performances.

(ii) Modify the desalting barrier by deposition of an additional polyamide layer; Test films and note effect on increasing salt retention.

(iii) Modify the composition of the of PVAL gel-layers by amine-modifications, either prior to or post membrane-making;

(iv) Test membranes for chlorine-tolerance;

(v) Later, establish technique for duplicating results on capillary membrane surfaces.

2. RO membranes from amine-containing precursors:

(a) Poly-2-vinylimidazoline (PVI) membranes:

(i) Synthesis, purification and characterization of PVI membrane-making materials and establishment of a technique of quality control for this novel polymeric precursor;

(ii) Making of membranes by the interfacial polycondensation method, using PVI and various crosslinking agents, and studying the effects of the numerous fabrication variables on membrane performances;

(iii) Evaluation of membranes, including testing with feed-water containing chlorine and feed-water of low- and high-pH.

(b) Polyvinylalcohol co-vinyl p-aminophenyl ether (PVACVAPE) membranes:

(i) Synthesis, purification and characterization of PVACVAPE;

(ii) Making of membranes from PVACVAPE, using different methods;

(iii) Testing of membranes for RO performances.

RESULTS AND CONCLUSIONS

1. Polyvinylalcohol (PVAL) membranes

Both flat-sheet and tubular PVAL membranes could be made by using either of three different insolubilization crosslinking techniques:

(i) heat treatment in the presence of H_2SO_4 as catalyst;

(ii) formation of blends of PVAL and maleic acid-*alt*-maleic acid anhydryde (MVE-*alt*-MAH) or;

(iii) insolubilization by crosslinking with potassium peroxydisulphate.

2. After extensive investigations into the effects of fabrication variables on membrane performances, the following typical results were recorded:

(a) PVAL/Δ H_2SO_4: 70 - 85%; (2 000 ppm NaCl, 2 MPa)
700 - 800 lmd
> 90%; (500 ppm $MgSO_4$, 2 MPa)
600 lmd

These results indicated that this membrane system could function as a medium retention and medium flux RO membrane at relatively low operating pressures, even in the absence of an additional interfacially formed salt-retention barrier.

(b) The performance of the PVAL/MVE-*alt*-MAH membrane varied with the pH of the feed solution, due to the fixed charge character of these membranes.

Membranes prepared from a solution with a specific ratio of components and heat cured in the presence of H_2SO_4 catalyst exhibited sufficiently high permeate flux for use as a gel sub-layer for RO membranes.

PVAL/MVE-*alt*-MAH; > 60% retention; (pH 11, 2 000 ppm NaCl, 2 MPa)
600 - 900 lmd

(c) PVAL - potassium persulphate ($K_2S_2O_8$) gel-layer membranes were created, suitable for nanofiltration applications. Many variables had an effect on membrane performance, most notable of which was the maturation time of PVAL/$K_2S_2O_8$ coating solutions.

Membranes made by the insolubilization of PVAL with $K_2S_2O_8$ (18 days maturation) gave the following typical performances:

50% retention; 480 lmd flux; (2 000 ppm NaCl, 2 MPa)
75% retention; 480 lmd flux; (1 000 ppm $MgSO_4$, 2 MPa)

3. The PVAL/$K_2S_2O_8$ membranes were evaluated on an industrial effluent of an oversaturated feed solution of Ca SO_4 (10 000 ppm $CaSO_4$), to study their long-term performance and ability to resist fouling. These membranes exhibited a retention of about 62% and flux of about 1 440 lmd and remained stable over a period of 600 h.

4. Laboratory tests on cooling-water blow-down from the SASOL II plant were also carried out with the PVAL/$K_2S_2O_8$ membranes, comparing them to CA membranes. Retentions of

the PVAL-based membranes ranged from 50 - 80% and fluxes of up to 240 lmd were recorded, after 40 h testing. CA membranes exhibited a significantly higher retention.

5. The crosslinked PVAL gel-membranes were then used as a base upon which polyamide membranes were deposited, to attain higher retention performance from PVAL-based membranes.

   (a) The deposition of an ultra-thin polypiperazine isophthalamide skin on the surface of an insolubilized PVAL sub-layer resulted in increased salt retention, but not without adverse effects on the permeate flux. Typical results of these membranes (PKPIP) are given below:

   80% retention; < 240 lmd flux; (2 000 ppm NaCl; 2 MPa; 20°C)
   75% retention; < 240 lmd flux; (1 000 ppm $MgSO_4$; 2 MPa; 20°C)

   (b) Composite UTF membranes could also be made without the insolubilization of the PVAL prior to the deposition of the polyamide skin. This could be achieved by the interfacial reaction of a mixture of PVAL and an amine (in aqueous solution) with a suitable multifunctional acid chloride (in an organic solvent). Good results were obtained by the reaction of an aqueous solution containing PVAL (0,25%), piperazine (0,25%) and NaOH (0,5%) with a solution of isophthaloyl chloride in hexane (1%)(PPIP membranes):

   > 80% retention; 960 lmd; (2 000 ppm NaCl; 3 MPa; 20°C)

6. The abovementioned membranes were of interest to Membratek, who required reasonably high-retention membranes for a certain local application.

   A selection of the amine-modified PVAL membranes PPIP (PVAL/PIP/IPC) were, together with modified PVI membranes, fabricated, first tested in the laboratory and then, after modularization, on cooling-water-blow-down (CWBD) for the SASOL II plant at Secunda.

   Although the RO performances of the laboratory tested membranes surpassed the requirements for that application, RO performances of the up-scaled membranes, in module form were below requirement. (This is discussed again later in point 9).

7. Poly-2-vinylimidazoline (PVI) can be used as precursor material in interfacial reactions to make efficient RO membranes. These could be made in flat-sheet and tubular forms. The use of PVI, with its nitrogen atoms being pendent to the hydrocarbon chain, resulted in some increase in chlorine-tolerance of the membranes. This chlorine-tolerance was greater than that of membranes made with the aliphatic polymeric precursor PEI (NS-100/1 membranes), but not as great as that of membranes made from the aromatic precursor phenylenediamine (FT-30 membranes).

   The optimum RO performances of PVI-OD/SCl tubular membranes (developed during a parallel study) were:

97,1 ± 0,1% retention; 730 ± 24 lmd
(tested for 2 000 ppm NaCl at 2 MPa)

The optimum RO performances of PVI-FD/SCI tubular membranes (developed during a parallel study) were:

97,1 ± 1,1% retention; 643 ± 74 lmd
(tested for 2 000 ppm NaCl at 2 MPa)

Initial results of "unoptimized" RO performances of PVI/CFD/SCI tubular membranes were:

97,0 ± 1,1% retention; 643 ± 74 lmd
(tested for 2 000 ppm NaCl at 2 MPa)

Exposure of PVI UTF membranes to chlorine is not advisable. It is, however, proposed that exposure of PVI-FD/SCI membranes to 5 ppm chlorine at pH 6 to 7 for a short period of time would be tolerated. Prolonged exposure to chlorine results in irreversible decline in retention.

Maximum performance of PVI-FD/SCI tubular membranes have been recorded in the pH 6,5 to 7 range. These membranes can be safely used over a pH range of 4,5 to 8,5.

8. By incorporation of various hydrophilic additives into a PVI-precursor solution: piperazine, PVAL or HA-1, UTF membranes were obtained which were considered adequate for low-pressure applications (< 2000 kPa).

   PVI FD-PVAL/SCI (CAMOH) membranes and PVI-FD + piperazine/SCI (CAMPIP) membranes exhibited stable performances over an extended test period of 200 h and which exceeded the performance of a PVI-FD/SCI control membrane: 90% retention and 200 lmd flux at 500 kPa applied pressure.

   CAMOH membranes and CAMPIP membranes were selected for modularization and testing on SASOL CWBD (together with the previously mentioned PVAL/PIP membranes). Individual test results on those tubular membranes surpassed the market requirements, but retention decreased after modularization (as discussed in point 9).

9. The Institute was approached by Membratek to supply PVAL membranes, then under development, for field trials by DEBEX Desalination. The objective was to desalinate brackish water to potable standard in compliance with SABS specifications. The feedwater contained $CaSO_4$ and NaCl at a TDS content of approximately 3 000 mg/l. The water was at a temperature of 38°C and contained no free chlorine. The membranes were required to have a high salt retention (> 90% NaCl) at relatively low pressures (2 - 3 MPa).

   PPIP (PVAL + PIP/IPC), CAMOH 5 and CAMPIP 3 membranes were supplied.

   Results showed that these membranes were up to specifications, when tested as single tubes (about 95% retention, 600 lmd at 3 MPa).

RO performances of the modules, however, was markedly lower; it decreased to about 40% retention, with a corresponding increase in flux.

This was found to be due to the failure of a few of the membrane tubes in the module. The cause of this failure is unknown at present; there is a possibility that it may be the module assembly technique.

10. The amine-modified PVAL material, PVACVAPE was, at length, synthesized and composite PVACVAPE/IPC membranes fabricated by various methods. Test results on early membranes have shown these membranes to have poor RO properties, especially low flux. The best results obtained, to date, were:

46% retention; 400 lmd; (2 000 ppm NaCl, 2 MPa)
90% retention; 400 lmd; (2 000 ppm $MgSO_4$, 2 MPa)

At this stage we have a good knowledge and understanding of the chemistry and membrane fabrication variables to make PVAL, amine-modified-PVAL, PVI and modified PVI membranes; most of which are repeatable and fulfil the contract requirements of: medium to high retention RO membranes and low to medium retention NF membranes.

For the sake of simplicity, a table has been drawn up to summarize the various types of membranes which have been investigated during this contract period, the progress made, action remaining to be taken and recommendations.

Summary of membranes studied:

Membrane code	Fabrication	Type	Performance	Stage reached, State of art/ Proposed action/Recommendations
PVAL/H_2SO_4	PVAL crosslinked by heat, with H2SO4 catalyst, to form PVAL gel-layer membranes	medium-retention, medium-flux RO	70-85%, 700-800 lmd (2 000 mg/l NaCl, 2 MPa), >90%, 600 lmd (500 mg/l MgSO4 , 2 MPa). After exposure to chlorine: no change in salt retention, moderate flux increase.	Reproducible flat-sheet and tubular membranes have been prepared. By changing fabrication conditions, adequate membranes for either RO or gel-layers can be created. Research terminated, and technology available.
PVAL/MVE-alt-MAH	Support membrane coated with blends of PVA + MVE-alt-MAH, crosslinking by heat treatment	Low retention RO	>60%, 600-900 lmd (pH 11, 2 000 mg/l NaCl, 2 MPa).	Blends with certain ratios gave membranes with sufficiently high permeate fluxes for use as gel-layers for RO membranes. Research terminated.
PVAL/$K_2S_2O_8$ (PK)	PVAL + K2S2O4 solutions, on PES, insolibilized by heat treatment	NF	50%, 960 lmd (2 000 mg/l NaCl, 2 MPa) 75%, 960 lmd (1 000 ppm, Mg4SO4, 2 MPa)	Reproducible PK membranes for NF made and available. Performance depends largely on solution maturation time. Membranes suitable for use as hydrophilic gel-layers for RO membranes. Membranes tested on CaSO4 slurry; resistant to abrasion, after 600 h. Single membranes tested on SASOL CWBD performed adequately. Propose study further effects of time of solution maturation on membrane performance.
PPIP	Crosslinking of precursor of PVAL + PPIP with IPC or TMC	Low-retention RO	>80%, 960 lmd (2 000 ppm, NaCl, 2 MPa)	Single membranes performed adequately on synthetic and SASOL (CWBD) feeds. PPIP Modules showed decreased performance. Investigate why modules failed and suggest solutions, e.g. new storage solutions, regeneration techniques.

Membrane code	Fabrication	Type	Performance	Stage reacted, State of art/ Proposed action/Recommendations
PPDAA	Crosslinking of precursor of PVAL + PDAA with IPC	-	Initial membranes: 46%, 450 lmd (2 000 ppm, NaCl, 2 MPa)	Much work remains to be done to improve the performance of this membrane. Suggest: (a) improvement in solubility of polyamide (b) preparation of PPDAA + PVAL copolymers to be used as precursors in membrane making.
PKPIP	Deposition of PIP/IPC amide barrier on insolubilized PVAL/$K_2S_2O_8$ gel layer	Low retention RO	80%, <240 lmd, (2 000 ppm, 2 MPa) 95%, <240 lmd, (1 000 $MgSO_4$, 2 MPa)	Good retention achieved, but very low fluxes led to discontinuation of study.
PVACVAPE/ IPC	Polymeric PVACVAPE cross-linked with IPC	-	46%, 400 lmd (2 MPa, 2 000 mg/l NaCl)	Discontinued due to combined low retention and low flux, and complicated synthesis of polymeric precursor.
PVI-OD/SCI	PVI-OD interfacially cross-linked with SCI	RO	Mathematically optimized tubular membranes: 97%, 730 lmd (2 000 mg/l NaCl, 2 MPa).	Research completed, except for ascertaining favourable membrane storage conditions prior to modularization.
PVI-FD/SCI	PVI-FD interfacially cross-linked with SCI	RO	Mathematically optimized membranes: 98,2%; 560 lmd (2 000 mg/l NaCl, 2 MPa)	Research completed, except for ascertaining favourable membrane storage conditions prior to modularization.
PVI-CFD/SCI	PVI-CFD interfacially cross-linked with SCI	RO	Unoptimized membranes: 97%, 640 lmd	Very good RO performances from early membranes. Research discontinued and membranes not optimized due to small quantities of PVI-CFD available to date.
CAM OH	Precursor of admix. of polymeric PVI + PVOH, crosslinked with SCI	RO	CAMOH 5: ± 97%, 1100 lmd (2 000 mg/l NaCl, 2 MPa) Retention and flux improved with time, CAMOH 3: 97-98,4%; 420-600 lmd after 200 h.	Performances depended on ratios of reactants. Research considered complete. Single membranes performed very well on synthetic and SASOL CWBD feeds, but modules showed decreased performance. Investigate why modules failed and suggest solutions (see PPIP membranes).

Membrane code	Fabrication	Type	Performance	Stage reacted, State of art/ Proposed action/Recommendations
CAM PIP	Precursor of admix. of PVI + monomeric PIP, crosslinked with SCI	RO	CAMPIP 3: ± 98%, 1100 lmd (2 000 mg/l NaCl, 2 MPa)	Performances depended on ratios of reactants: Research considered complete. Single membranes performed very well on synthetic and SASOL CWBD feeds, but modules showed decreased performance. Investigate why modules failed and suggest solutions (see PPIP membranes).

RECOMMENDATIONS FOR FURTHER RESEARCH

Recommendations for future research will basically be to investigate and, where possible, satisfy the local South African market requirements for adequate and improved membranes for water treatment; to prevent or correct environmental pollution and to improve the handling of industrial discharge.

New applications for membranes should also be investigated and membranes tailor-made to meet the demands of these new requirements. More specifically, membranes for bio-reactors and chemical processes, such as ozonolysis of potable water, should be investigated.

Throughout future research, under- and post-graduate students will continue to be trained in the membrane-related aspects of water-treatment technology. It is recommended that we become more involved in co-operative programmes with other researchers and institutions in South Africa, and possibly overseas; together striving to create membranes of improved performances, capable of meeting the market requirements, and to broaden the acceptability, use and applications of desalination membranes.

Examples of proposed interactive projects include:

(i) Studying of the applicability of our membranes to Membratek's module technology;

(ii) Preparation of precursor polymers for the making of membranes from specialized organic chemical compounds: - high oxidation and chlorine resistant diacids and hydrophilic furan resins, with Prof. D. Schneider, Department of Chemistry, University of Stellenbosch (currently underway in Dept. Chemistry);

(iii) Supplying of adequate quantities of membrane - making chemicals to our parallel project, of Dr. Ed Jacobs, for their making of membranes in long length capillaries and large modules;

(iv) Modification of surfaces of PES substrates for use in the making of higher flux UTF composite membranes, together with Dr. G. Summers of Vista University, Port Elizabeth.

Further to the aforementioned, recommended fields of investigation at IPS, include:

(i) Preparation of modified phenolics for the regeneration of sub-standard and degraded membranes by an *in situ* treatment. Results will be applied at Eskom on operating plants;

(ii) Investigation into the formulation of tougher cellulose acetate derivatives for use in preparing RO, UF and nanofiltration membranes; this will be in collaboration with the parallel membrane production research project. It will be necessary for the viscosity of cellulose derivative solutions to be modified to match spinning requirements and structures must be modified to control final membrane microstructure;

(iii) Continuation of the extensive programme concerning polyvinylalcohol membranes for use in treatment of SASOL CWBD streams and potable water treatments, in conjunction with Debex Desalination;

(iv) Further modification of PVAL membranes for improved RO performances and reasonable chlorine tolerance and bacterial resistance;

(v) Preparation of fluorinated microfilter membranes for ozone distribution in ozonators and for ozone degradation of organic wastes;

(vi) Preparation of polyacrylonitrile and carbon membranes for bioreactors, the carbon membrane having ultraporous surface structures;

(vii) Preparation of hydrophilic polymer surfaces, for instance, polypropylene, gluable by epoxy and wettable by water. (Early results have been very good.)

LIST OF CONTENTS

LIST OF FIGURES

Figure 16:	Effect of persulphate concentration on NaCl retention at different pressures
Figure 17:	Effect of curing time on permeate flux at different pressures. (Solution 1 at 80 °C)
Figure 18:	Effect of curing time on NaCl retention at different pressures. (Solution 1 at 80 °C)
Figure 19:	Effect of curing time on permeate flux at different pressures. (Solution 2 at 80 °C)
Figure 20:	Effect of curing time on NaCl retention at different pressures. (Solution 2 at 80 °C)
Figure 21:	Effect of curing time on permeate flux at different pressures. (Solution 1 at 60 °C)
Figure 22:	Effect of curing time on NaCl retention at different pressures. (Solution 1 at 60 °C)
Figure 23:	Effect of curing time on permeate flux at different pressures. (Solution 2 at 60 °C)
Figure 24:	Effect of curing time on NaCl retention at different pressures. (Solution 2 at 60 °C)
Figure 25:	Effect of solution maturation on permeate flux at different persulphate concentrations
Figure 26:	Effect of solution maturation on NaCl retention at different persulphate concentrations
Figure 27:	Effect of solution maturation on permeate flux at different persulphate concentrations
Figure 28:	Effect of solution maturation on $MgSO_4$ retention at different persulphate concentrations
Figure 29:	Effect of solution maturation on permeate flux at different pressures
Figure 30:	Effect of solution maturation on NaCl retention at different pressures
Figure 31:	Effect of solution maturation on permeate flux at different pressures
Figure 32:	Effect of solution maturation on $MgSO_4$ retention at different pressures
Figure 33:	Effect of solution maturation on permeate flux at different pressures
Figure 34:	Effect of solution maturation on NaCl retention at different pressures
Figure 35:	Effect of solution maturation on permeate flux at different pressures
Figure 36:	Effect of solution maturation on $MgSO_4$ retention at different pressures
Figure 37:	$CaSO_4$ flux and retention versus running time

PART B:

LIST OF TABLES

PART B

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1. INTRODUCTION

The rapidly expanding population of the world is placing a great strain on available water supplies. As in some other parts of the world, South Africa has arid regions and is faced with the additional hardship of periodic droughts.

Present groundwater resources in the Republic are estimated to be adequate for only the next 30 years, whereafter the demand will exceed supply. The time has therefore come for conventional sources of water supply in selected areas to be supplemented by means of advanced techniques applied to wastewater purification to meet the future increase in demands for water of both adequate quality and quantity.

A number of processes has been developed, worldwide, for obtaining usable or potable water by desalination of seawater and brackish water. These processes include: distillation, freezing, ion-exchange and the membrane-based operation of reverse osmosis (RO). Membrane process can also make a valuable contribution to restore or improve the quality of water resources and aqueous effluent streams. As such, they offer a viable technology for the re-use of water, be it through the possibility of recycling which they offer or merely improving the quality of discharge effluent.

1.1 REVERSE OSMOSIS

Since the early 1970s, desalination by the pressure-driven membrane process of RO has developed into a commercially viable process. RO has become increasingly favoured as a separation process because it consumes far less energy than other processes do. Reverse osmosis is a process for the separation of substances in a solution. It is the process whereby water is forced, by pressure, through a semipermeable membrane, counter to the normal direction of osmotic flow.

The heart of the RO process is the semipermeable membrane which must allow passage of the water but not of the dissolved solids. Both the chemical nature and porous substructure of the membrane surface together govern the mechanism of RO separation.

Historically, cellulose acetate (CA) has been the most important polymer used in the development of membranes suitable for reverse osmosis applications. More recently, ultra thin film (UTF) composite membranes, comprising a thin semipermeable film deposited onto a finely porous ultrafiltration (UF) supporting membrane, have been produced by interfacial polymerization, or *in situ* polymerization. The following table (Table A) lists some of the commercially available RO membranes which have been developed:

TABLE A:

Commercial RO membranes and modules

Company	Membrane material	Starting Materials	Membrane Type	Designation	Module Type
Membratek	CA	Cellulose acetate	Asymmetric	-	Tubular
Desal	CA PA	Cellulose acetate	Asymmetric Composite	- -	Spiral-wound
Du Pont	CA Aramid Aramid	Cellulose acetate	Composite Composite Asymmetric	- - -	Spiral-wound Spiral-wound Hollow-fibre
FilmTec	PA Polyurea Furan	1,3-Diaminobenzene + TMC PEI + TDI Furfuryl alcohol + sulphuric acid	Composite Composite Composite	FT-30 NS-100 NS-200	Spiral-wound
UOP Fluid Systems	PA-300 RC-100	Epiamine + IPC => polyetheramide Epiamine + TDI => polyetherurea	Composite Composite	TFC-803 TFC-801	 Spiral-wound
DDS	CA PA	Cellulose acetate	Asymmetric Composite	- -	Plate & Frame
PCI	CA PA	Cellulose acetate	Asymmetric Composite	AFC Range CPA; CDA	Tubular
Nitto Denko	PA/PVAL	Amine + PVAL + IPC/TMC	Composite	NTR-729; NTR-739; NTR-7250	Spiral-wound Tubular Capillary
Sumitomo	PAN	Polyacrylonitrile	Asymmetric	-	Spiral-wound
Toray	CA PA	Cellulose acetate THEIC + furfurylalcohol PIP or aromatic amine (X-linked)	Asymmetric Composite Composite	- PEC-100 UTC	Spiral-wound
Toyobo	CA	Cellulose acetate	Homogeneous	-	Capillary
Osmonics	CA Polyfuran	Cellulose acetate -	Asymmetric Integrated	- -	Spiral wound Spiral
Koch Membrane Systems	CA PS	Cellulose acetate Polysulphone	-	-	Tubular RO (tolerant)

CA = Cellulose acetate
PA = Polyamide
PVAL = Polyvinyl alcohol
PAN = Polyacrylonitrile
TMC = Trimesoyl chloride
PEI = Polyethyleneimine
TDI = Toluene diisocyanate
THEIC = 1,3,5-tris(hydroxyethyl)isocyanuric acid
PIP = Piperazine

Desalination features of further commercially available RO membranes are described in: "Membrane Processes" by R. Rautenbach and R. Albrecht, J. Wiley and Sons, Switzerland (1989), pp. 34-37.

1.2 NANOFILTRATION

Nanofiltration (NF) is a term that has recently been introduced to describe a membrane process that is distinguished by the differential retention of ions. It is a pressure-driven process that lies between conventional RO and UF, since the pore size of NF membranes (1 - 15 nm) lies between that of RO (arguably no pores) and UF (5 - 20 nm). The salt-retention mechanism of NF membranes may be due to one or more forces, namely, charge (coulombic) interaction, hydrated-ion size-exclusion, or dielectric interaction. A typical NF membrane, such as the Film Tec XP45, has an NaCl retention of 50% and an $MgSO_4$ retention of 97,5%. When these results are compared with those of a typical RO membrane (Film Tec FT30) which has retentions of 98% and 99% for NaCl and $MgSO_4$ respectively, and a typical UF membrane that does not reject these salts at all, the distinction between the three membrane types, namely, RO, NF and UF, is clear. NF membranes are mainly employed in water softening operations, as these low-pressure membranes show a higher selectivity towards divalent, rather than monovalent ions, in feed solutions of mixed ion contents. These membranes may also be used in the removal of low molecular mass organic species from waste streams.

1.3 MOTIVATION

The steady rise over the years in the world-wide installed capacity of pressure-driven membrane operations, reflects the increased acceptance by industry of these operations for treatment of aqueous streams: both for water and/or product recovery, for the treatment of effluents and for the production of potable water.

The same trend had been observed in South Africa, where there has been a slow, but steady, expansion in the use of pressure-driven membrane operations in water purification applications, both in the spheres of water supply and effluent treatment. Illustrative of this, amongst other examples, is the production of potable water from brackish borehole-supplies at Bitterfontein, and the use of membranes for salt removal to improve the water balance at the Lethabo power station. These are based on Cellulose Acetate (CA) membrane technology.

It must be expected, however, that the present, well established, CA membrane technology must have a finite life. New and improved membranes are required and these will not only add new technological advantages, but will be able to replace existing membranes in existing plants. Almost all commercial membranes to date, especially the high-retention amine-type membranes, show a limited tolerance towards the presence of chlorine. In the search for new and improved membranes for RO and related applications, attention must therefore be given to the incorporation of tolerance into the membranes, by chemical modifications of, and to, membrane materials.

1.4 OBJECTIVES

The main objective of this contract was to generate a family of low-pressure thin-film membranes, useful for water desalination. Two classes of membranes were to be considered:

(a) a medium to high NaCl-retention reverse osmosis (RO) membrane, exhibiting 85 - 95% retention at operating pressures of 1 500 - 2 000 kPa, and

(b) a low to medium NaCl-retention nanofiltration (NF) membrane, exhibiting 40 - 60% retention at operating pressures of 500 - 1 000 kPa.

These membranes were to be made after carefully studying, the chemistry of various polymeric materials and with consideration for the many variables which pertain to the making of synthetic membranes.

The following types of synthetic membranes were selected for investigation and the following studies were conducted:

1. Polyvinylalcohol (PVAL) membranes:

   (i) Evaluate different techniques and reagents to produce insoluble PVAL films;
   Test films for RO and/or UF performances.

   (ii) Modify the desalting barrier by deposition of an additional polyamide layer;
   Test films and note effect on increasing salt retention.

   (iii) Modify the composition of PVAL gel-layers by amine-modifications, either prior to - or post-membrane-making;

   (iv) Test membranes for chlorine-tolerance;

   (v) Later, establish a technique for duplicating results on capillary membrane surfaces.

2. RO membranes from amine-containing precursors:

(a) Poly-2-vinylimidazoline (PVI) membranes:

   (i) Synthesis, purification and characterization of (PVI) membrane-making materials and establishment of a technique of quality control for this novel polymeric precursor;

   (ii) Making of membranes by the interfacial polycondensation technique, using PVI and various crosslinking agents, and studying the effects of the numerous fabrication variables on membrane performances;

   (iii) Evaluation of membranes, including testing with feed-water containing chlorine and feed-water of low and high pH.

(b) Polyvinylalcohol-co-vinyl p-aminophenyl ether (PVACVAPE) membranes:

   (i) Synthesis, purification and characterization of PVACVAPE;

   (ii) Making of membranes from PVACVAPE using different methods;

   (iii) Testing of membranes for RO performances.

PART A

2. POLYVINYLALCOHOL MEMBRANES

2.1 INTRODUCTION AND OBJECTIVES

The research which was conducted was at aimed at the development of poly(vinyl alcohol) [PVAL]-based composite RO membranes for desalination of aqueous salt solutions with low osmotic pressures, such as brackish water and industrial waste water. The suitability of these PVAL-based composite membranes for nanofiltration applications was also considered.

The research approach entailed preparing such composite membranes by depositing an aqueous solution of PVAL and a crosslinking/insolubilization agent onto a porous poly(arylether sulphone) [PES] substrate membrane and then insolubilizing the PVAL coating to create a stable hydrophilic gel layer. An ultrathin salt-retention barrier on top of the PVAL gel layer could also be created to increase salt retention.

Since the inception of non-cellulosic thin-film composite membranes in the 1970s, a number of polymers have been investigated as possible RO membrane materials. At the present time commercially available RO membranes comprise mainly cellulose acetate (CA) (degree of acetylation 2,5 - 2.8) and, to a lesser extent, a family of aromatic polyamides.

Both the CA and polyamide-based membranes suffer from a number of practical drawbacks. On the one hand CA membranes are intolerant of feed waters that are too alkaline or too acid and are susceptible to microbial attack under certain circumstances. The polyamide membranes suffer, by and large, from a lack of resistance to chlorine in the feed waters. A continuing need also exists for improvements in compaction resistance, stability over a wide pH range, dry-storage stability and stability at elevated temperatures. Most commercially available membranes fall short of meeting at least one or more of the above requirements.

Polyvinyl alcohol (PVAL) is a material with good chemical and thermal stability, as well as having a high permeability to water. Moreover, PVAL has the ability to form films when cast from aqueous solution [1]. PVAL appears to be an attractive membrane-producing material. However, PVAL is very hydrophilic, leading to the permeation of both water and hydrated salts, and water soluble. In order to create a good membrane structure, therefore, PVAL needs to be modified.

As our long-term research objective was to develop thin-film composite PVAL-based RO membranes for desalination of brackish water and industrial waste-water, the final PVAL-based composite membrane must have high water permeability and adequate salt-retention capability at low operating pressures of $\leq$ 2 MPa. It should also exhibit good chemical resistance (preferably chlorine resistance), thermal stability up to 70°C, and hydrolytic stability.

When membranes are formed directly on a porous substrate by interfacial polymerization of multifunctional monomers, it is difficult to completely cover fine pores on the substrate and defects are easily caused. Researchers at Nitto [2] showed that problems with low water permeability and reproducibility of membrane performance could be overcome if an inner layer of water-insoluble PVAL was present between the porous substrate and the ultrathin polyamide skin layer.

It was initially decided to follow an approach similar to that of Nitto company, but instead of a simultaneous crosslinking and polymerization of PVAL and amino compounds, we chose to prepare the intermediate PVAL gel layer and the ultrathin salt-retention barrier in two separate steps. The initial phase of our research therefore focused on the controlled *in situ* insolubilization of the intermediate PVAL layer using various methods. The primary objective was to prepare mechanically stable, high-flux gel sublayers for RO membranes. However, the potential use of these insolubilized PVAL membranes, alone, in RO applications has been investigated by monitoring the effect of fabrication variables on their salt-retention capability.

The following were the objectives of the research programme:

(i) The first phase focused on various ways to insolubilize the PVAL membrane coating, thereby creating a permanent gel-layer membranes.

(ii) Consideration was to be given to further chemical modifications of gel-layer membranes in order to enhance their salt-retention and water permeability characteristics for a particular application.

(iii) In order to improve the salt-retention properties of PVAL membranes, methods for the formation of composite UTF-membranes comprising different polyamide skins on the PVAL gel-sublayer were investigated. Several different membrane types were made and evaluated for performance.

(iv) A further phase of the program included investigation into synthesis of partially modified PVAL (amine modified) and the formation of ultrathin salt-retention barriers on PVAL gel-layers by interfacial polycondensation.

2.2 LITERATURE SURVEY

Several methods have been developed to make very thin synthetic membranes. Only two of these have become technologically important, namely, (i) the original approach of Loeb and Sourirajan [3] for the preparation of asymmetric membranes by the solvent-nonsolvent phase-inversion process, and (ii) the method of interfacial polymerization [4]. When carried out at one surface of a porous support material, this polymerization technique is widely used commercially as a means of producing thin-film composite (RO) membranes.

During the last two decades, primary emphasis in nonpolysaccharide membrane research and development has focused on aromatic polyamides and other related rigid, nitrogen-containing, hydrophilic heterochain polymers, e.g., aromatic polyhydrazides and polyureas [5]. Although a wide variety of materials exist to choose from for RO applications, the various aromatic polyamides in integrally skinned (asymmetric) and interfacially formed composited membrans have, for many years, been the most attractive candidates on the basis of their performance and cost. These membranes exhibit water permeability and salt-retention characteristics, as well as thermal, biological, and chemical resistance properties, superior to those of conventional asymmetric cellulose acetate membranes.

As a result of their inherent chain rigidity and a low extent of water-induced swelling, these aromatic backbone polymers exhibit low water permeabilities and, consequently, the membranes have to be operated at high transmembrane pressures (6 - 10 MPa) to obtain useful water fluxes. This makes them unsuitable for desalination of aqueous salt solutions with low osmotic pressures, such as brackish water and industrial wastewater, where permeate fluxes of at least 500 lmd (liters per square meter per day) are required at low operating pressures of $\leq$ 2 MPa.

Another shortcoming that has limited the broader use of nitrogen-containing thin-film composite membranes in desalination applications is the lack of resistance to attack by chlorine and other oxidizing agents present in the feedwater. Over the years, several attempts have been made to develop chlorine-resistant membranes by using non-nitrogen containing polymers as membrane materials. Properties such as chemical stability, film-forming ability, and high hydrophilicity make poly(vinyl alcohol) (PVAL) an attractive material for production of RO membranes.

The chemical stability of PVAL has been tabulated in Table 1.

<u>TABLE 1</u>:

The chemical stability of PVAL at 25°C [1]

Reagent	Concentration (%)	pH	Membrane material			
			PVAL	PVB	PVAc	CA
HNO_3	12	0	3	0	0	0
H_2SO_4	48	0	3	0	0	0
HCO	7	0	3	0	0	0
NH_4OH	25	13	3	0	0	0
NaOH	10	14	3	0	0	0
Phenol	0.1	3	3	0	0	0
Phenol	1.0	3	3	0	0	0
Phenol	2.0	3	3	0	0	0
Ethanol	100	7	3	0	0	0
DMF	100	7	3	0	0	0
DMSO	100	7	3	0	0	0
Formamide	100	7	3	0	0	0

Degrees of stability: 0, destruction of the membrane; 1, strong swelling, deterioration, 2, little swelling, still usable; 3, stable, no alteration.

Abbreviations: PVAL, polyvinyl alcohol; PVB, polyvinylbutyrate, PVAc, polyvinylactate; CA, cellulose acetate.

The high hydrophilicity of PVAL, however, leads to permeation of both water and hydrated salts. To create stable membranes with good mechanical properties, and to improve the selective permeability to water and salts, the PVAL must be insolubilized by crosslinking or other modification reactions.

The insolubilization of PVAL can be affected in a variety of ways. A few of the more relevant reactions are listed below.

Formation of complexes with inorganic compounds and metal ions

> This includes the formation and decomposition of the chromate ester of PVAL, the reaction of PVAL with boric acid and borax, and the complexation of PVAL with copper salts. The latter two reaction products are sensitive to pH changes.

The reaction of PVAL with dialdehydes

> PVAL can be crosslinked with dialdehydes such as glyoxal, glutaraldehyde and terephthaladehyde. This type of reaction is commonly used in the preparation of PVAL-based alkaline battery separators. Both inter- and intramolecular acetalization reactions are possible.

Dehydration of PVAL in the presence of mineral acids

> The PVAL gel layer can be insolibilized by means of an acid-catalyzed dehydration reaction. Dehydration of PVAL by sulphuric acid can result in double-bond formation through β-elimination.

Insolubilization of PVAL in the presence of peroxidisulphate

> Peroxidisulphates, such as potassium persulphate, have been widely used as initiators of aqueous vinyl polymerizations. Apart from being a source of free radicals, peroxidisulphates are known to be strong oxidizing agents in an aqueous medium [5-10].

Earlier work on PVAL membranes focused on the water and salt permeability of dense (homogeneous) films, e.g. those prepared by heat treatment [11] and formalization of preformed PVAL membranes [12]. In recent years, there has been a great deal of interest in both asymmetric and thin-film composite PVAL-based RO membranes. The separation and flow capabilities of asymmetric PVAL membranes have been studied extensively by Peter and Stefan [13-17]. They prepared asymmetric membranes from PVAL and some of its derivatives by the classical phase-inversion method, using various types of precipitation solutions. The water-soluble membranes were insolublized by crosslinking with solutions of organic compounds containing aldehyde, ketone, or carboxylic acid groups or with polyvalent metal ions, such as Cr^{3+}. The crosslinked membranes exhibited good chemical, mechanical, and thermal resistance and were designed for the removal of phenol and organic solvents from toxic industrial wastewater.

Katz and Wydeven [18-20] studied the water and salt transport characteristics of asymmetric PVAL membranes that were stabilized by ionizing radiation [18,19] and heat treatment [19,20] and proposed a method for preparing thin-skinned, high-flux PVAL membranes. The characteristics of these asymmetric membranes were controlled by the casting conditions and by the post treatment methods used. Chang [21] prepared asymmetric PVAL membranes by the phase-inversion method, using various precipitation baths. The membranes were crosslinked with formaldehyde. The retention of various mono- and divalent cations and anions by these membranes were investigated to determine which ions could be separated from wastewater.

Brannon and Peppas [22] developed a new procedure for forming asymmetric PVAL membranes by the phase-inversion method. Their membranes were formed by casting a PVAL solution on a glass plate, drying the solution at 40°C, and pouring a precipitation solution, consisting of $(NH_4)_2SO_4$, $ZnCl_2$, $Na_2SO_4 \cdot H_2O$, and deionized water, over the PVAL coating. The system was covered to prevent evaporation. The phase-inversion process was followed by crosslinking. For this purpose, the precipitation solution was poured off and replaced by a crosslinking solution consisting of H_2SO_4, glutaraldehyde, methanol, and acetic acid; the system was again covered and heated at 40°C for 4 h to facilitate crosslinking. The correlation between the structure of these asymmetric membranes and solute transport through them was studied using theophylline and vitamin B_{12}.

Porous PVAL-poly (vinyl acetate) (PVA_c) composite membranes, although not with an asymmetric structure, were prepared by Hayashi [23] et al. They extracted PVAc with organic solvents from PVAc latex films that were obtained by emulsion polymerization of VAc in the presence of PVAL. Permselective asymmetric polymer blend membranes were prepared by Tsuchihara and co-workers [24] using a mixture of aqueous PVAL, PVAc emsulsion, and LiCl. Tsuchihara et al. [25] also reported the use of blends of PVAL and cyanoethylated PVAL for membrane preparation.

Cadotte et al. [26] investigated the preparation of thin-film composite RO membranes by *in situ* crosslinking of PVAL coatings on porous polysulphone supports. Aldehyde crosslinking agents, such as formaldehyde, glyoxal, acrolein, and terephthalaldehyde, as well as compounds such as hexamethoxymethyl melamine and 2-formyl-5-furansulphonic acid were used. The RO properties of these membranes were tested at very high operating pressures on 3.5% synthetic sea water. Koyama et al. [27-29] prepared interpolymer anionic composite RO membranes by depositing a solution of PVAL (as membrane matrix) and poly(styrene sulphonic acid)(as polyelectrolyte) on a microporous polypropylene support, evaporating the solvent and heat-curing the membrane at 120°C. Infrared spectra of heat-cured membranes suggested that crosslinking occurred by formation of $R—O—SO_2—R$ bonds between the two polymers, as well as by intermolecular dehydration of PVAL during heat-curing in the presence of poly(styrene sulphonic acid). The retentions of NaCl [27], polar organic solutes, e.g., alcohols, phenols, monocarboxylic acids, amines, and ketones [28], and phenolic derivatives [29] by these thin-film composite membranes were studied.

Jian and Ming [30] reported the formation of thin-film composite RO membranes by coating a polysulphone support with aqueous solutions of PVAL, containing aliphatic dicarboxylic acids (e.g., oxalic, malonic, and crosslinking the PVAL membranes by heat treatment at 90 - 120°C. Wojciak and Voelkel [31] previously reported that, in the absence of H_2SO_4 catalyst, dense PVAL membranes could not be crosslinked with malonic or succinic acids in the temperature range 80 - 120°C. Heat-resistant composite semipermeable membranes were prepared at Nitto Electric Industrial Co. [32] by coating a microporous polytetrafluoroethylene support with an aqueous solution of PVAL and H_2SO_4 catalyst, heating the membrane at 150°C, then coating it with an aqueous solution of poly(acrylic acid) and H_2SO_4 catalyst, and heating it again at 160°C. This composite membrane exhibited high NaCl retentions and relatively low water fluxes at an operating pressure of 40 kg cm^{-2}.

Linder et al. [33] prepared thin-film composite desalination membranes by coating a microporous polypropylene support with a solution of PVAL, or vinyl alcohol copolymers, which had been treated with a reactive dye. The composite membrane was dried and heated in a Na_2CO_3 solution to crosslink and fix the dye-modified PVAL membrane. Researchers at Toray Industries [34] made thin-film composite RO membranes by coating an aqueous solution, containing PVAL, hydroquinone, and sodium lauryl sulphate (as surfactant), on a porous polysulphone support and contacting the PVAL/hydroquinone coating with an organic solution of trimesoyl chloride to give an interfacially polymerized membrane. After drying and heat treatment, the membrane was coated with a 20% aqueous PVAL solution and heated again to give a high-retention, low-flux composite membrane useful for sea water desalination (3,5% NaCl feed).

Ikehata et al. [35] prepared composite membranes by coating a porous polypropylene support with an aqueous solution of PVAL and NaOH and heating the PVAL membrane at 80°C for 5 h to form a water-insoluble PVAL coating. This composite membrane exhibited very high water permeability and was used for ultrafiltration purposes. Thin-gel composite membranes for bioseparations were reported by Li and Barbari [36]. They coated PVAL solutions on a porous cellulose acetate support and crosslinked the PVAL interfacially by reacting it with an organic solution of isophthalaldehyde. Himeshima and Uemura [37] made semipermeable composite membranes, used in low-pressure desalination applications, by crosslinking PVAL with divinylsulphone on a porous polypropylene support.

In the preparation of chlorine-resistant PVAL-based membranes for low-pressure desalination of brackish water and industrial wastewater, the most successful approach so far has been of preparing thin-film composite membranes comprising (i) a porous subtrate, (ii) an ultrathin salt-retention barrier formed by interfacial crosslinking and polymerization of PVAL and an amino compound having at least two secondary amino groups with a multifunctional reagent that reacts with the secondary amino groups and the hydroxyl groups of PVAL, and (iii) an inner layer of water-insoluble PVAL that is present between the porous substrate and the ultra thin film. This procedure, developed by Nitto Electric Industrial Co. in Japan, has been described extensively in the patent literature [38-40].

Typically, a porous polysulphone support is coated with an aqueous solution of PVAL, piperazine, and NaOH as acid acceptor, then dipped into a hexane solution of trimesoyl chloride, dried, and heat-treated at 110°C. In a slight variation of this procedure, aromatic diamines, e.g., *m*-phenylene diamine, are used instead of cycloapliphatic secondary diamines [41]. A similar approach has been followed by researchers at Sumitomo Chemical Co. [42], but they used poly(ethylene glycols) and other polyhydroxy compounds instead of PVAL.

The RO performance of Nitto's NTR-7250 chlorine-resistant membranes in brackish water desalination applications has been discussed by Kamiyama et al.[43] These thin-film composite PVAL-based membranes exhibited high $MgSO_4$ retentions, but low NaCl retentions. After the NTR-7250, Nitto developed the NTR-729 and NTR-739 HF (high flux) series membranes [44]. These are thin-film composites made from modified PVAL. They exhibit excellent chlorine resistance, high water flux, and high NaCl retention in brackish water desalination, even at low pressure of 1 MPa.

The development of PVAL membranes has been tabulated in Table 2. (References to this table have been included with the original table (Table 2.7, reference 45).

TABLE 2:
Development of PVAL membranes

YEAR	NAME	FABRICATION TREATMENT	PROCESS	MEMBRANE PERFORMANCE		
			TEST CONDITIONS		RETENTION (%)	FLUX (lmd)
1973	C.T.Chen *et al.*	Formalization; dense film	RO, Desalination	1000 ppm NaCl; 25 ^{o}C; 4.2 MPa	92	3.3
1975	Y.Nozawa *et al.*	Alkali bridging				
1975	R.Dick *et al.*	Diisocyanate				
1976	S.Peter *et al.*	Cr^{3+}	RO, Desalination	2000 ppm phenol; 25 ^{o}C; 5 MPa	79	50
1976	S.Peter *et al.*	Boric acid; Cr^{3+}	RO, Desalination	2000 ppm phenol; 25 ^{o}C; 5 MPa	86	70
1977	T.Uragami *et al.*	Alkali bridging				
1977	S.Peter *et al.*	Cr^{3+}; Glutaraldehyde	RO, Desalination	2000 ppm phenol; 25 ^{o}C; 5 MPa	95	30
1978	T.Uragami *et al.*	Alkali bridging	UF	1% PEG 1000; 40 ^{o}C; 5 MPa	40	30
1978	T.Uragami *et al.*	Alkali bridging	UF	1% PEG 4000; 40 ^{o}C; 5 MPa	100	28
1978	S.Peter *et al.*	Organic comp.'s; metal salts	RO, Desalination	2000 ppm phenol; 25 ^{o}C; 5 MPa	96	80
1980	K.Koyama *et al.*	PVAL/PSSA + heat	RO, Desalination	5000 ppm NaCl; 8 MPa	88-93	9-28
1980	NITTO	PVAL + PIP + TMC + heat	RO, Desalination	500 ppm MgSO$_4$; 1.4 MPa	98	1250
1981	M.G.Katz *et al.*	Heat treatment; asymmetric	RO, Desalination	1800 ppm NaCl; 30 ^{o}C; 7 MPa	83	560

YEAR	NAME	FABRICATION TREATMENT	PROCESS	MEMBRANE PERFORMANCE		
			TEST CONDITIONS		RETENTION (%)	FLUX (lmd)
1981	S.Peter *et al.*	Ketones	RO, Desalination	2000 ppm phenol; 25 °C; 5 MPa	73	100
1981	S.Peter *et al.*	Dicarboxylic acids	RO, Desalination	2000 ppm phenol; 25 °C; 5 MPa	74	60
1981	S.Peter *et al.*	Dialdehydes	RO, Desalination	2000 ppm phenol; 25 °C; 5 MPa	99	90
1981	M.G.Katz *et al.*	Gamma radiation	RO, Desalination	1000 ppm NaCl; 25 °C; 7 MPa	35	high
1982	M.G.Katz *et al.*	Heat treatment; symmetric	RO, Desalination	1800 ppm NaCl; 30 °C; 7 MPa	78	30
1982	Ho Nam Chang	Formalization	RO, Desalination	1800 ppm NaCl; 25 °C; 5 MPa	30	60
1982	T.Tsuchihara *et al.*	Cyanoethylation				
1983	T.Wydeven *et al.*	$CuSO_4$	RO, Desalination			50
1983	T.Wydeven *et al.*	$CuSO_4$; heat treatment	RO, Desalination			50
1983	Wang Ying *et al.*	Boric acid; oxalic acid; cr^{3+}	RO, Desalination	3000 ppm phenol; 25 °C; 5 MPa	90	5000
1983	W.Wojciak *et al.*	Dicarboxylic acids				
1983	NITTO	H_2SO_4 + heat + PAN + heat	RO, Desalination	5000 ppm NaCl; 4 MPa	96	420
1984	NITTO	PVAL + diamine + TMC	RO, Desalination	500 ppm $MgSO_4$	98	980
1985	W.Chiang *et al.*	Maleic anhydride; heat				
1986	T.Uragami *et al.*	Glutaraldehyde				

YEAR	NAME	FABRICATION TREATMENT	PROCESS	MEMBRANE PERFORMANCE		
			TEST CONDITIONS		RETENTION (%)	FLUX (lmd)
1986	A.Higuchi *et al.*	PVAL-co-IA				
1986	NITTO	PVAL + diamines + IPC/TMC	RO, Desalination	5000 ppm $MgSO_4$	90-99	800-1250
1987	M.L.Brannon *et al.*	$ZnCl_2$; glutaraldehyde				
1987	T.Hirotsu *et al.*	Photochemical				
1987	S.Jian *et al.*	Dicarboxylic acids	RO, Desalination	3500 ppm NaCl; 25 °C; 4 MPa	95	120
1987	M.Miura	Gamma radiation				
1987	NITTO	PVAL + PDA + TMC + heat	RO, Desalination	2000 ppm NaCl; 25 °C; 1 MPa	97	1000
1989	Y.Himeshima *et al.*	Divinylsulphone	RO, Desalination	1500 ppm NaCl; 25 °C; 0.75 MPa	15	330
1993	E.IMMELMAN et al.	Sulphuric acid + heat	RO, Desalination	2000 ppm NaCl; 25 °C; 2 MPa	80	400
1993	E.IMMELMAN et al.	Persulphate + heat	RO, Desalination	2000 ppm NaCl; 25 °C; 2 MPa	60	650
1993	E.IMMELMAN et al.	PVAL + PVME-alt-MA	RO, Desalination	2000 ppm NaCl; 25 °C; 2 MPa	60	600-900

PEG = Polyethylene glycol
PVAL = Polyvinyl alcohol
PSSA = Polystyrene sulphonic acid
PIP = Piperazine

MA = Maleic anhydride
PVME = Polyvinyl methyl ether
PDA = m-Phenylene diamine
IPC = Isophthaloyl chloride

PAN = Polyacrylonitrile
TMC = Trimesoyl chloride
IA = Itaconic acid

POLYAMIDE MEMBRANES

Polyamide ultra thin film (UTF) membranes are prepared by the interfacial reaction of multifunctional amines with multifunctional acid chlorides contained in immiscible solvents. Typically, a microporous support is dipped into an aqueous solution of a monomeric, oligomeric, or polymeric amine, drained of excess solution, and then dipped into the multifunctional crosslinking agent in an organic solvent. An acid scavenger is usually added to the aqueous solution to neutralize the HCl condensate resulting from the polycondensation reaction. After a second drainage step, the polymeric film formed at the interface of the two solutions is heat-cured to effect complete crosslinking.

Examples of amines used in the production of commercially available membranes include piperazine (PIP) and its oligomeric derivatives, polyethyleneimine (PEI), ethylenediamine (EDA), diethylenetriamine (DETA), and diaminobenzene (DAB). Isophthaloyl chloride (IPC) and trimesoyl chloride (TMC) are the crosslinking agents most commonly employed. Table 3 lists some of the commercially available polyamide membranes.

TABLE 3:

Composition and RO performance of various polyamide membranes

Membrane Designation	Reactants Active layer	Test Conditions	Retention (%)	Flux (lmd)
NS-101 (PA-100)	PEI + IPC	35000 ppm NaCl 10337 kPa; 25 °C	99,3	1200
PIP	PIP + IPC	35000 ppm NaCl 10337 kPa; 25 °C	98,0	840
NS-300 Family	PIP + TMC	35000 ppm NaCl 10337 kPa; 25 °C	98,0	800
	PIP oligomer + IPC+TMC	35000 ppm SSW 10337 kPa; 25 °C	99,0	530
FT-30	DAB + TMC	35000 ppm SSW 6891 kPa; 25 °C	99,4	1200
UTC-70	Aromatic polyamide with carboxylate groups	1500 ppm NaCl 1500 kPa; 25 °C	>99,5	1300
2N31	Ethylenediamine + TMC	1000 ppm NaCl 5513 kPa; 25 °C	96,9	320

IPC = Isophthaloyl chloride
TMC = Trimesoyl chloride
PIP = Piperazine
PEI = Polyethyleneimine
DAB = 1,3-Diaminobenzene
SSW = Synthetic seawater

Table 3 shows that the polyamide membranes exhibit salt-retention properties comparable to asymmetric cellulose acetate membranes (Retention > 99%; Flux = 560 lmd at 2 MPa), and that they are suitable for many RO desalination applications. There remain, however, several problems associated with the fabrication and RO characteristics of polyamide UTF membranes. These problems can be ascribed to the chemical and physical nature of the ultra-thin polyamide films deposited on the substrate, and include:

(a) The difficulty in obtaining a homogeneous polyamide film that is physically bound to the substrate, covers all the pores of the substrate, and has no defects such as pin-holes or hairline cracks. NORTH STAR suggested the use of a rubber roller to remove the excess amine solution prior to the interfacial reaction. This ensures that the polymer film is formed at the immediate surface and in the pores of the support. The use of this method is, however, limited to the preparation of flat-sheet membranes, and the method cannot be used to fabricate tubular or capillary membranes.

(b) The fragility of the UTF membranes and their susceptibility to damage when handled during the assembly of modules.

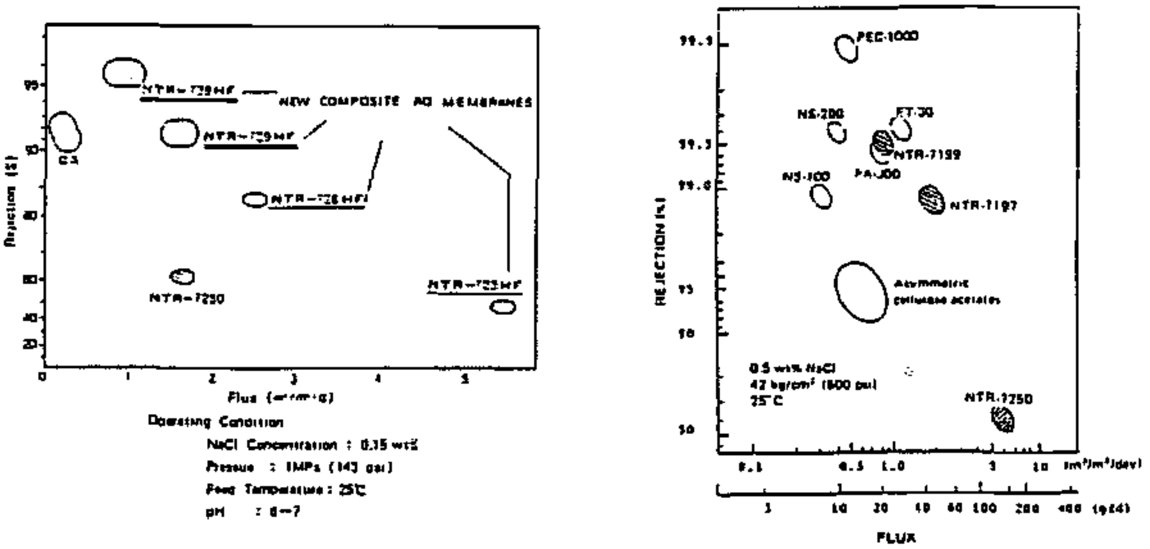
(c) The decline in performance of some of these membranes under corrosive conditions due to hydrolysis of the amide bonds. The choice of the amine and acid chloride used in the interfacial polycondensation reaction is of the utmost importance in determining the chemical stability of the membrane. Tertiary amide linkages are regarded to be much more stable than secondary amide linkages toward hypochlorite attack [46].

PVAL/PA MEMBRANES

It has been shown that an insolubilized gel-layer of PVAL deposited between the support membrane and the polyamide desalination barrier can solve many of the problems which arise in the preparation of polyamide UTF membranes [2]. The PVAL gel-sublayer covers the relatively large pores of the UF membranes used as a support, and, in turn, acts as an excellent support for the fragile ultra-thin polyamide membrane. The NITTO ELECTRICAL INDUSTRIAL CO. LTD. used di- and trifunctional acid chlorides to crosslink PVAL and difunctional secondary amines on PS supports to form UTF composite RO membranes. These membranes are reported to have excellent chlorine resistance and desalination properties at low pressures.

In a typical NITTO process, a porous PS support was coated with an aqueous solution containing PVAL 0,5, PIP 0,5, and NaOH 0,95 m%. The support was then immersed in a crosslinking solution containing 2,0 m% TMC in a 60:40 (weight ratio) heptane - diethyl ether mixture for 1 min at 25 °C. After evaporation of the solvent, the coated material was heated at 110 °C for 10 min to complete the crosslinking reaction. Variations of this process include the use of other amines (derivatives of piperazine or difunctional aromatic amines) and other crosslinking agents, such as IPC.

RO results obtained with Nitto's NTR-729, NTR-739, NTR-7250 membranes believed to be made by the techniques described above, are shown in Figure 1.



<u>**FIGURE 1**</u>:
Performance of NITTO low-pressure membranes compared with that of other commercial RO membranes [43, 44]

2.3 INSOLUBILIZATION OF PVAL GEL SUBLAYERS

2.3.1 INSOLUBILIZATION BY ACID-CATALYZED DEHYDRATION

2.3.1.1 Background

Thermal Degradation of PVAL

A discussion pertaining to this topic has been included in the publication:
Poly(vinyl alcohol) gel sublayers for Reverse Osmosis Membranes 1. Insolubilization by Acid-Catalyzed Dehydration, included in Addendum 1.

The physical properties of PVAL are to a large extent dependent on the polymerization conditions of the parent PVAc and the hydrolysis conditions, which determine the composition of the final product. Commercially available grades of PVAL must, in fact, be regarded as copolymers of vinyl alcohol (VA) and vinyl acetate (VAc), since they usually correspond to a hydrolysis degree of 70 - 99%. Therefore, the thermal degradation behaviour of PVAL will depend on sample characteristics (e.g., molecular weight and degree of hydrolysis, as well as method of hydrolysis). Experimental conditions, such as heating rate, the

2.3.1.2 Materials and Methods

Chemicals

Poly(arylether sulphone) [VICTREX 4800G, a product of ICI, England] was used for the formation of asymmetric substrate membranes. Partially hydrolyzed PVAL (degree of hydrolysis 86-89%; average molecular mass 72 000) was purchased from SAARCHEM. Concentrated sulphuric acid (98%) was used as dehydration catalyst. Salt-retention capabilities of dehydrated PVAL gel layers were determined using NaCl (CP grade) and hydrated $MgSO_4$ (CP grade) feed solutions.

Membrane Fabrication

Tubular (13 mm diameter) and flat-sheet substrate membranes were manufactured in-house by the phase-inversion deposition of poly(arylether sulphone) [PES] on a poly(ethylene terephthalate) non-woven fabric [Viledon^{TM} : Carl-Freudenberg, Germany]. Substrate membrane materials and optimization of membrane fabrication variables have been developed and reported in detail by Jacobs [52].

PVAL was dissolved in distilled water by continuous stirring for a period of 24 hours. All solutions were filtered before use to remove undissolved particles. Flat-sheet composite membranes were prepared by depositing aqueous PVAL solutions on PES substrates, using a technique which will be referred to as dip-coating. Typically, the substrate membrane was first drained of excess water for 2 min, then immersed in an aqueous PVAL/H_2SO_4 solution for 5 min, removed and drained of excess PVAL solution for 5 min. The membrane coatings were then heat treated in an oven at 100 - 125°C for 10 - 30 min to effect insolubilization. Four membranes were prepared from each coating solution. Variables that were studied in an attempt to optimize the reverse osmosis performance of the composite membranes included PVAL concentration, H_2SO_4 concentration, wetting, draining and curing times, as well as curing temperature. The compositions and fabrication conditions of flat-sheet membranes are given in Table 4.

TABLE 4:

Compositions of coating solutions and membrane fabrication conditons:
Flat-sheet PVAL/H_2SO_4 membranes

Membrane No.	PVAL Conc. (mass %)	H_2SO_4 Conc. (mass %)	Wetting time (min.)	Draining time (min.)	Curing time (min.)	Curing temp. (°C)
A.1 - A.4	0.5	0.2	5	5	20	120
A.5 - A.8	1.0	0.2	5	5	20	120
A.9 - A.12	2.0	0.2	5	5	20	120
B.1 - B.4	2.0	0.1	5	5	20	125
B.5 - B.8	2.0	0.2	5	5	20	125
B.9 - B.12	2.0	0.5	5	5	20	125
C.1 - C.4	2.0	0.5	5	5	10	125
C.5 - C.8	2.0	0.5	5	5	20	125
C.9 - C.12	2.0	0.5	5	5	30	125
D.1 - D.4	2.0	0.5	5	5	20	100
D.5 - D.8	2.0	0.5	5	5	20	110
D.9 - D.12	2.0	0.5	5	5	20	125
E.1 - E.4	2.0	0.1	5	5	20	125

PVAL/H_2SO_4 coatings were also deposited on 13 mm tubular PES substrate membranes. The compositions of the coating solutions and the membrane fabrication conditions are summarized in Table 5.

TABLE 5:

Compositions of coating solutions and membrane fabrication conditions:
Tubular PVAL/H_2SO_4 membranes

Membrane Code	LP-1	LP-2	LP-3	LP-4	LP-5	LP-6	LP-7	LP-8
PVAL (mass %)	1.0	2.0	1.0	2.0	1.0	2.0	1.0	2.0
H_2SO_4 (mass %)	0.4	0.4	0.8	0.8	0.4	0.4	0.8	0.8
Substrate predraining time (min)	5	5	5	5	5	5	5	5
Wetting time (min)	5	5	5	5	5	5	5	5
Draining time (min)	5	5	5	5	5	5	5	5
Curing time (min)	20	20	20	20	20	20	20	20
Curing temp. (°C)	110	110	110	110	130	130	130	130

These membranes were cured in a vertical updraft oven, which permitted an even distribution of heat and, consequently, much better control over the extent of dehydration. The effects of PVAL concentration, H_2SO_4 concentration and curing temperature on RO properties were investigated.

Evaluation of Membrane Performance

A schematic representation of the membrane evaluation equipment is shown in Fig. 2.

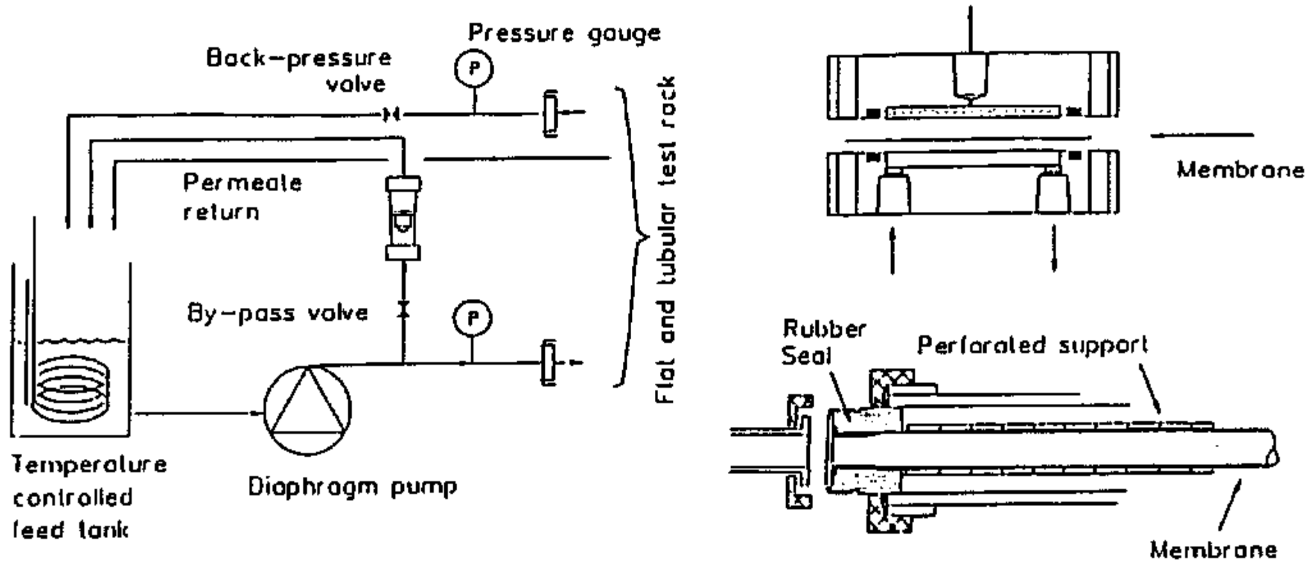


FIGURE 2:
Schematic diagram of membrane evaluation equipment

Testing conditions for the individual experiments are indicated in the tables and figures in the RESULTS AND DISCUSSION (section 2.3.1.3). Typically, flat-sheet membranes were tested at 2 MPa, pH 6.5 and 25°C on either a 2000 mg/l NaCl or a 500 mg/l MgSO4 feed solution. Tubular membranes were tested at 2 MPa, pH 6.0 and 20°C on a 2000 mg/l NaCl feed solution, unless stated otherwise. The salt-retention and permeate flux values are defined as follows:

$$\text{Retention} = 1 - \frac{\text{Conductivity of permeate}}{\text{Conductivity of feed}} \times 100\ (\%)$$

$$\text{Flux} = \frac{\text{Volume of permeate recovered}}{\text{Membrane area} \times \text{Time}} \quad \text{(lmd: litres per square meter per day)}$$

In order to allow the salt-retention and flux values to stabilize, a period of between 22 and 24 hours elapsed between the start-up time and the time at which the first permeability measurements were taken.

Chlorine treatment

The effect of chlorine treatment on the RO performance of both flat-sheet and tubular membranes was investigated by using sodium hypochlorite (NaOCl) as the source of active chlorine. Flat-sheet composite membranes (prepared by dip-coating a PES support with an aqueous solution of 2% PVAL and 0,5% H_2SO_4 and heating the membranes at 120°C for 20 min) were immersed in an aqueous solution of 250 mg/l NaOCl at pH 6,0 and 25°C. After an exposure time of 6 h, the membranes were removed and evaluated in RO experiments.

In the case of tubular PES-PVAL composites, membranes LP-1 to LP-8 (shown in Table 5) were first evaluated in RO experiments on a NaCl feed solution. After 75 h of operation, the feed tank was rinsed and filled with distilled water. The temperature of the water was adjusted to 20°C, the pH was adjusted to a value of 6,0, and the membranes were shock-treated with chlorine by adding 350 mg/l NaOCl to the feedwater. After running the membranes on NaOCl solution for 6 h, NaCl (200 mg/l) was again added to the feedwater. The salt-retention and flux values were measured at regular intervals over a period of 120 h to monitor changes in membranes performance. The chlorine shock treatment was repeated after a total operating time of 200 h.

2.3.1.3 Results and Discussion

Reverse Osmosis Performance of Flat-Sheet Composite Membranes

Effect of PVAL Concentration

Table 6 shows the salt retention and permeate flux as a function of PVAL concentration. Moderate increases in salt-retention capability were observed when the concentration was increased from 0,5 to 2%. The flux values obtained for membranes consisting of 2% PVAL were considerably lower than those obtained for membranes prepared from 0,5% polymer solution. An increase in the polymer concentration results in an increase in membrane thickness, with a corresponding decrease in the rate of water transport.

TABLE 6:

The effect of PVAL concentration on RO properties[a] of flat-sheet membranes

	PVAL Concentration (Mass %)											
	0.5				1,0				2,0			
	Membrane No.[b]											
	A.1	A.2	A.3	A.4	A.5	A.6	A.7	A.8	A.9	A.10	A.11	A.12
Retention (%)	49.4	46,6	44.5	47.1	56.8	53.4	55.4	59.2	60,4	61,8 ·	63.4	62.0
Permeate Flux (lmd)	1598	1621	1628	1611	1541	1570	1566	1519	1091	1085	1025	1081

a. Membranes tested at 25°C. pH 6.5. and 2 MPa on 2000 mg/l NaCl feed.

b. See Table 4 for fabrication conditions.

Effect of Sulphuric Acid Concentration

The effect of H_2SO_4 concentration on reverse osmosis performance is shown in Table 7. As the H_2SO_4 concentration increased, the salt retention of the membranes increased, while the flux values decreased correspondingly. Commercial grades of PVAL are usually produced by alkaline hydrolysis and therefore contain some residual sodium acetate. It is known that sodium acetate also promotes dehydration of PVAL on heating, resulting in discolouration of films [53]. Apparently, the addition of an equivalent amount of H_2SO_4 greatly reduce the rate of discolouration, but any excess promotes acid-catalyzed dehydration. Since sulphuric acid presumably acted only as catalyst, and not as reactant, concentration was not expected to play such a significant role. The increase in salt retention with increasing concentration of H_2SO_4 seems to indicate that a higher acid concentration increases the rate of dehydration at a specific temperature. Therefore, it is possible that similar levels of salt retention could be achieved if membranes with lower acid contents are heated for much longer periods of time.

TABLE 7:

The effect of H_2SO_4 concentration on RO properties[a] of flat-sheet membranes

	H_2SO_4 Concentration (Mass %)											
	0.1				0.2				0.5			
	Membrane No.[b]											
	B.1	B.2	B.3	B.4	B.5	B.6	B.7	B.8	B.9	B.10	B.11	B.12
Retention (%)	55,1	54,0	51.3	52.2	60,8	65.8	59,7	62,4	77,1	81,6	75,4	78,1
Permeate Flux [lmd]	1518	1560	1588	1526	997	978	1017	1015	817	761	825	802

a. Membranes tested at 25°C, pH 6,5, and 2 MPa on 2000 mg/l NaCl feed.
b. See Table 4 for fabrication conditions.

Effect of curing time

Table 8 shows the effect of curing time on reverse osmosis properties of flat-sheet composite membranes. It is evident that excessive curing times (longer than 20 min at 125°C) resulted in considerable decreases in water flux, without a significant increase in salt retention.

TABLE 8:

The effect of curing time on RO properties[a] of flat-sheet membranes

	Curing Time (min)											
	10				20				30			
	Membrane No.[b]											
	C.1	C.2	C.3	C.4	C.5	C.6	C.7	C.8	C.9	C.10	C.11	C.12
Retention (%)	53,4	47.2	51,0	48,4	76,1	79,3	80,1	76,2	83.7	81.6	83.2	81,0
Permeate Flux (lmd)	1266	1332	1298	1321	822	797	774	835	254	311	271	345

a. Membranes tested at 25°C, pH 6.5, and 2 MPa on 2000 mg/l NaCl feed.
b. See Table 4 for fabrication conditions.

Effect of curing temperature

The effect of curing temperature on salt retention and permeate flux is shown in Table 9. The rate of water elimination is expected to be strongly dependent on heat-treatment temperature. Temperatures in excess of 130°C were considered to be undesirable, because of the detrimental effect that prolonged heat treatment at high temperatures could have on the asymmetric pore structure of the PES substrate membranes. In the temperature range studied (100 - 125°C), it appears as though a curing temperature of around 125°C gave the tightest membrane with the highest salt retention and the lowest flux. However, flux values of about 800 lmd for membranes cured at 125°C were regarded as quite promising.

TABLE 9:

The effect of curing temperature on RO properties[a] of flat-sheet membranes

	Curing Temperature (°C)											
	100				110				125			
	Membrane No.[b]											
	D.1	D.2	D.3	D.4	D.5	D.6	D.7	D.8	D.9	D.10	D.11	D.12
Retention (%)	61.5	59,1	60.2	58,0	67,2	68.1	68,5	72,8	77,0	81,1	74,1	79,7
Permeate Flux (lmd)	1098	1218	1185	1234	963	941	952	851	821	774	833	789

a. Membranes tested at 25°C, pH 6.5, and 2 MPa on 2000 mg/l NaCl feed.
b. See Table 4 for fabrication conditions.

Tables 6 to 9 show clearly that a simple manipulation of one or two variables could lead to PVAL gel-layer membranes with widely differing salt retention and water permeability characteristics.

Effect of operating pressure

The effect of operating pressure on salt retention and permeate flux is shown in Table 10. In this experiment, the H_2SO_4 content was only 0.1% and therefore salt retentions at 2 MPa were relatively low. As expected, permeate flux varied linearly with operating pressure. The flux values obtained at 2 MPa for this particular coating formulation were very promising, while the fluxes measured at 1 MPa were still useful.

TABLE 10:
The effect of operating pressure on RO properties[a] of flat-sheet PVAL membranes

	Pressure (MPa)											
	0.5				1.0				2.0			
	Membrane No.[b]											
	E.1	E.2	E.3	E.4	E.5	E.6	E.7	E.8	E.9	E.10	E.11	E.12
Retention (%)	41,2	34,5	35,3	38,4	48,6	40,7	42,1	46,2	57,2	49,3	51,3	54,0
Permeate Flux [lmd]	341	425	386	374	699	816	789	777	1488	1770	1588	1576

a. Membranes tested at 25°C, pH 6,5, and 2 MPa on 2000 mg/l NaCl feed.
b. See Table 4 for fabrication conditions.

Effect of pretreatment

The RO performances of dehydrated PVAL membranes which were subjected to various pretreatments are summarized in Table 11.

TABLE 11:
Reverse Osmosis performance[a] of PVAL/H_2SO_4 flat-sheet membranes[b] after various pretreatments[c]

	Membrane No.			
	1[c]	2[c]	3[d]	4[d]
Retention (%)	68.7	63.7	70.5	83.6
Flux (lmd) at 2 MPa	1655	1688	768	827
Retention (%)	60.9	56.6	67.5	74.9
Flux (lmd) at 1 MPa	817	916	323	373
Retention (%)	49.8	44.9	67.2	71.8
Flux (lmd) at 0.5 MPa	483	543	180	215
Retention (%) after 70 h	68.0	62.7	81.6	82.9
Flux (lmd) at 2 MPa after 70 h	1742	1848	761	924

a. Membranes tested at 25°C and pH 6.5 on a 2000 mg/l NaCl feed solution.
b. PVAL (M_w 72,000): 2%; H_2SO_4: 0.5%; membranes wetted for 5 min, drained for 5 min, and cured for 20 min at 125°C.
c. Membranes 1 and 2 pretreated with chlorine before evaluation of RO performance.
d. Membranes 3 and 4 not treated with chlorine. Membrane 3 was dry-stored for a few days at room temperature; membrane 4 was stored in distilled water for 24 h before being tested.

Membranes 1 and 2 were immersed in a solution of sodium hypochlorite (350 mg/l) at pH 6.0 for a period of 6 hours before evaluation of RO performance. After an operating time of 70 hours at 2 MPa, the NaCl retention capability of these membranes remained unchanged, while the permeate flux increased. In the case of the dry-stored membrane (no. 3), the salt retention increased by about 10% after 70 hours of operation, while the permeate flux remained unchanged. The NaCl retention of the wet-stored membrane (no. 4) remained unchanged, while the flux increased markedly.

Membranes 3 and 4 exhibited similar salt retentions after 70 hours of operation, but the flux of the wet-stored membrane was considerably higher than that of the dry-stored membrane. Although membranes subjected to chlorine pretreatment exhibited lower salt retentions, the fluxes were twice as high as those of untreated membranes. These results are not yet finalized and further investigations of the effect of storage conditions and chlorine pretreatment are being conducted.

$MgSO_4$ retention

The retention of divalent ions by the membranes shown in Table 11 was also investigated. For this purpose, the 2000 mg/l NaCl feed solution was replaced with a 500 mg/l $MgSO_4$ solution. The RO properties measured at 2 MPa are shown in Table 12. $MgSO_4$ retentions of up to 92% were obtained.

TABLE 12:

$MgSO_4$ retention[a] of PVAL/H_2SO_4 flat-sheet membranes[b] at 2 MPa, after various pretreatments[c]

Membrane No.	Retention (%) 6 h	Flux (lmd) 6 h	Retention (%) 18 h	Flux (lmd) 18 h
1	83.0	1375	83.3	1330
2	78.4	1548	78.6	1498
3	90.1	541	91.2	525
4	91.3	620	91.7	600

a. Membranes tested at 25°C and pH 6.5 on a 500 mg/l $MgSO_4$ feed solution.
b. See Table 11.
c. Pretreatments summarized in Table 11.

Membranes pretreated with chlorine exhibited much higher fluxes than the untreated membranes. In another experiment conducted with $MgSO_4$ as feed solution, the membranes were not subjected to any pretreatments, but were tested immediately after manufacture. The results are shown in Table 13.

TABLE 13:
MgSO$_4$ retention[a] of PVAL/H$_2$SO$_4$ flat-sheet membranes[b] at 2 MPa

Membrane No.	Retention (%) 6 h	Flux (lmd) 6 h	Retention (%) 18 h	Flux (lmd) 18 h
1	73.5	868	74,1	844
2	69,8	924	70.2	891
3	76,1	822	77.0	796
4	70,8	902	71,4	870

a. Membranes tested at 25°C and pH 6,5 on a 500 mg/l MgSO$_4$ feed solution.
b. PVAL (M_ω 72,000): 2%; H$_2$SO$_4$: 0,1%; membranes wetted for 5 min, drained for 5 min, and cured for 20 min at 125°C.

The concentration of H$_2$SO$_4$ used in this experiment was 0.1%, compared with 0.5% for membranes shown in Table 11. The lower salt retentions can therefore be explained in terms of a lower extent of dehydration.

Reverse Osmosis Performance of Tubular Composite Membranes

The salt retentions and fluxes of these membranes, tested at different operating pressures before and after shock-treatment of the membranes with chlorine, are given in Table 14.

TABLE 14:
Reverse osmosis performance[a] of tubular PVAL/H$_2$SO$_4$ membranes at different operating pressures

		Membrane Code							
Hours		LP-1	LP-2	LP-3	LP-4	LP-5	LP-6	LP-7	LP-8
Before chlorine treatment									
66	Flux (lmd) at 2 MPa	410	537	293	339	360	365	285	291
	Retention (%)	54.3	50.9	58.4	57.7	56.4	56.4	65.9	64.3
69	Flux (lmd) at 1.5 MPa	293	377	163	230	291	250	194	199
	Retention (%)	46.8	41.6	50.0	49.5	49.1	47.9	56.0	55.2
71	Flux (lmd) at 0.5 MPa	79	107	50	63	70	69	53	55
	Retention (%)	19.5	18.9	24.8	24.1	23.0	22.0	28.2	27.5
After first chlorine treatment									
81	Flux (lmd) at 2 MPa	438	606	348	357	428	386	300	306
	Retention (%)	61.1	59.0	62.5	62.5	61.7	61.2	68.6	67.6
146	Flux (lmd) at 1.5 MPa	410	543	357	355	421	373	293	303
	Retention (%)	55.2	51.7	56.8	56.3	55.8	55.8	63.3	60.1
173	Flux (lmd) at 2 MPa	492	620	435	438	516	466	339	360
	Retention (%)	56.7	53.8	58.7	58.0	57.7	57.7	65.0	62.1
176	Flux (lmd) at 1.5 MPa	373	465	314	318	350	339	248	283
	Retention (%)	50.5	47.4	52.0	51.5	51.5	51.5	58.7	55.9
194	Flux (lmd) at 1 MPa	243	301	199	204	227	205	159	170
	Retention (%)	38.8	35.3	40.5	40.3	40.0	40.0	46.5	44.3

196	Flux (lmd) at 0.5 MPa	100	127	81	84	96	85	67	71
	Retention (%)	20.7	18.1	22.9	21.4	20.9	21.2	24.9	23.9
After second chlorine treatment									
241	Flux (lmd) at 0.5 MPa	123	145	106	106	114	110	79	84
	Retention (%)	22.7	22.5	24.0	24.0	22.7	23.3	27.3	24.9
313	Flux (lmd) at 0.5 MPa	145	160	130	130	134	120	91	95
	Retention (%)	19.7	19.7	22.4	22.1	20.8	20.8	24.7	22.6

a. Membranes tested at 20°C and pH 6.0 on a 2000 mg/l NaCl feed solution.

Effect of fabrication variables

There were no significant differences between the RO properties of membranes LP-1 to LP-8. However, if LP-1 and LP-2 are compared with LP-7 and LP-8, it is evident that high H_2SO_4 concentrations and high curing temperatures resulted in lower fluxes and higher salt retentions. Membranes LP-3 and LP-4 (0.8% H_2SO_4; cured at 110°C) exhibited lower NaCl retentions and slightly higher fluxes than LP-7 and LP-8 (0.8% H_2SO_4; cured at 130°C), which shows that temperature plays a significant role in the dehydration reaction.

The fluxes obtained with tubular membranes were markedly lower than those obtained with flat-sheet membranes. This phenomenon can probably be attributed, at least in part, to the fact that casting solution compositions and fabrication conditions used for the preparation of flat-sheet PES substrate membranes differed considerably from those used in the manufacture of tubular substrates. For example, the PES concentration and casting solution viscosity were considerably higher in the case of tubular membranes. This usually results in membranes with more dense asymmetric structures, which in turn could affect water permeability.

The random selection of substrate membrane recipes in this study does, in fact, not permit a comparison of the two membrane systems. Therefore, the RO characteristics of flat-sheet PES-PVAL composite membranes cannot be extrapolated to the tubular membrane system. It is obvious that any attempt to optimize the reverse osmosis properties of the PVAL gel layer will have to include a simultaneous optimization of the PES substrate properties.

Effect of operating pressure

Figure 3 shows the effect of operating pressure on the RO properties of some tubular membranes. It is evident that the NaCl retention increased asymptotically to an equilibrium value, although this value was not yet reached at 2 MPa. Permeate flux increased linearly with increasing operating pressure. At pressures below 2 MPa, the fluxes were too low to be of practical use.

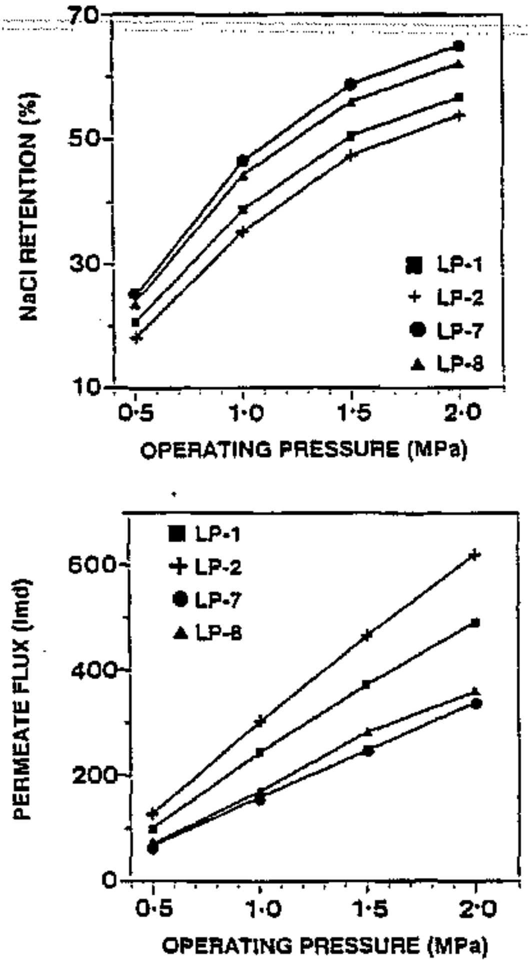


FIGURE 3:
Effect of operating pressure on (a) NaCl retention and (b) permeate flux of dehydrated PVAL tubular membranes (2 000 mg/l NaCl, 20°C, pH 6,0)

Effect of chlorine shock-treatment

Chlorine is commonly used as a disinfectant in water treatment. In RO systems, chlorine may be added to feedwater for control of micro-organisms and, in addition, to prevent membrane fouling by microbiological growth. Hence, the resistance of membrane-forming polymers to chlorine attack is always an important consideration in the development of RO membranes. It is common practice to study the interaction of chlorine and other halogen compounds with RO membranes by monitoring the decline in membrane performance.

Chemical attack on RO membranes by chlorine is in some cases revealed by an increase in permeate flux, accompanied by increasing salt permeability. This is evidently related to the breaking of chemical bonds within the polymer. In other cases membranes respond to chlorine attack by showing of decreased permeate flux, which can probably be attributed to halogen addition to these polymers, resulting in increased hydrophobicity.

In an aqueous solution, the reaction of NaOCl with acid results in the liberation of chlorine. The latter reacts with water to produce several chemical species, as shown in eqns. (1) and (2).

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (1)$$

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (2)$$

The distribution of the chlorine species in aqueous solution depends on pH and equilibrium constants for the above reactions. In acidic solution, Cl_2 and HOCl are the most chemically active species.

The RO properties of tubular membranes before and after chlorine shock-treatment are shown in Figure 4.

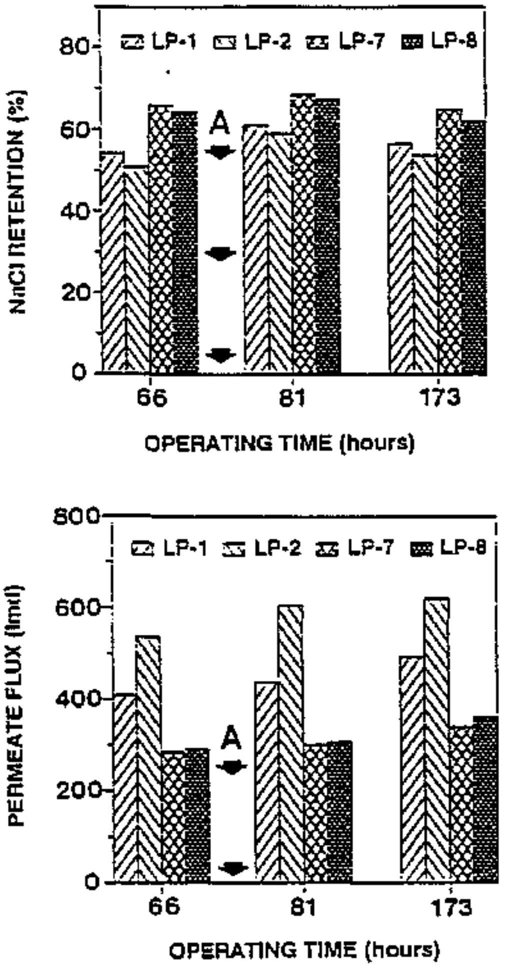
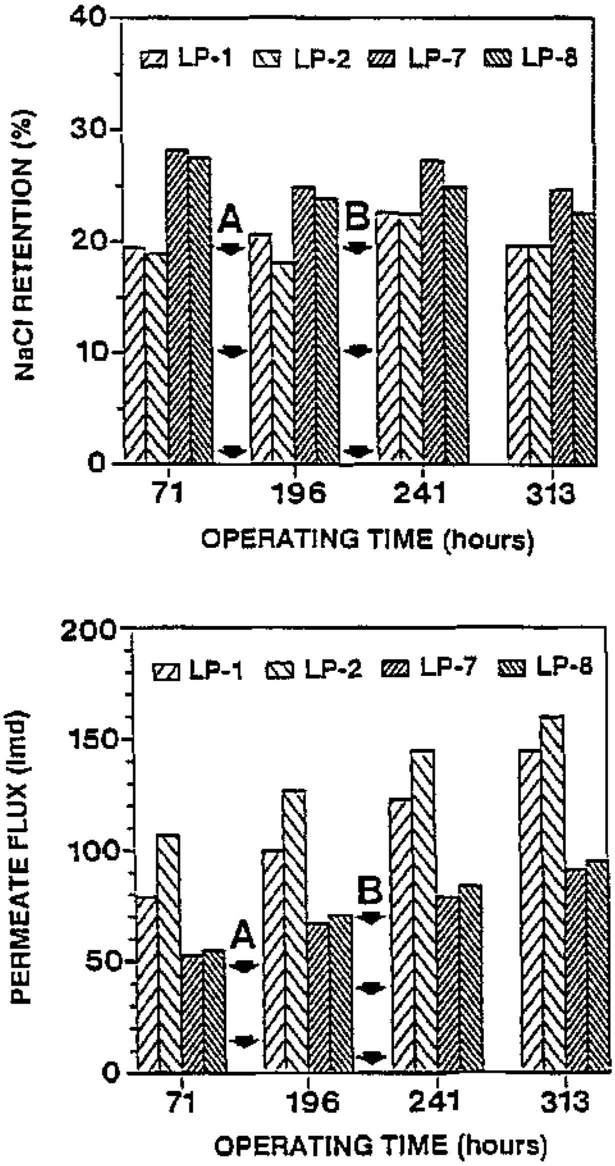


FIGURE 4:
Effect of operating time on (a) NaCl retention and (b) permeate flux of dehyrated PVAL tubular membranes tested at 2 MPa before and after chlorine shock treatments. Testing conditions: 20°C; pH 6.0; 2 000 mg/l NaCl feed. (A) Chlorine treatment after 75 h.

The NaCl retentions at 2 MPa increased slightly after addition of chlorine, but no significant changes in salt retention were observed over a period of 100 hours (i.e., retentions after 175 hours of operation were similar to those measured before chlorine shock-treatment). Moderate flux increases occurred after chlorine shock-treatment during the same period (Fig. 4b).

The RO performances of membranes tested at 0.5 MPa before and after chlorine treatments are shown in Figs. 5a and 5b.



<u>FIGURE 5</u>:

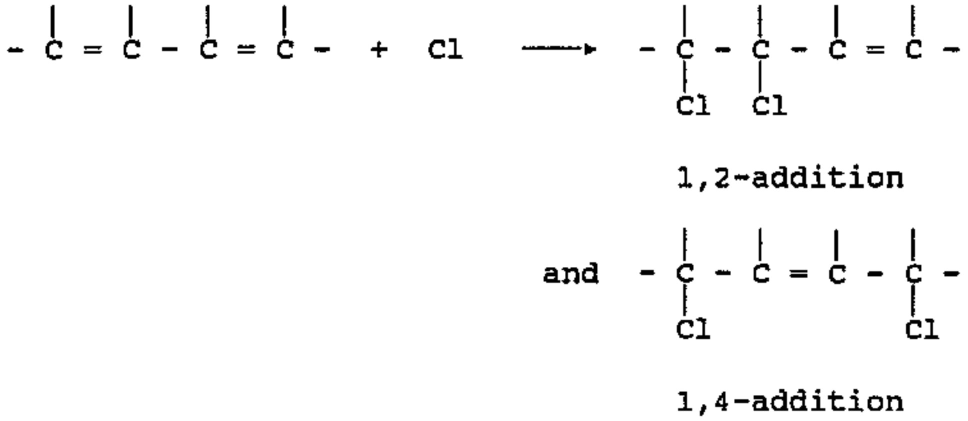
Effect of operating time on (a) NaCl retention and (b) permeate flux of dehyrated PVAL tubular membranes tested at 0,5 MPa before and after chlorine shock treatments. Testing conditions: 20°C; pH 6,0; 2 000 mg/l NaCl feed. (A) First chlorine treatment after 75 h; (B) Second chlorine treatment after 200 h.

After two chlorine shock-treatments, the retentions measured after about 310 hours of operation did not differ much from the values obtained before chlorine treatment (Fig. 5a). However, the permeate fluxes increased markedly over the same period (Fig. 5b). The RO performances of these tubular membranes were not adequate enough to justify the effort of monitoring the concentration of available chlorine in the feed solution as a function of time.

Since the dehydrated PVAL contains sequences of conjugated double bonds, and possibly also some isolated double bonds, the carbon-carbon double bond is the functional group in this polymer.

Dehydrated PVAL will therefore undergo reactions typical of alkenes and dienes, namely electrophilic and free-radical additions. In the present study, chlorine treatment of membranes was carried out at low temperature in aqueous solution and in the absence of a free-radical source. Therefore, only electrophilic additions of Cl_2 and HOCl (the most chemically active species) to carbon-carbon double bonds need to be considered.

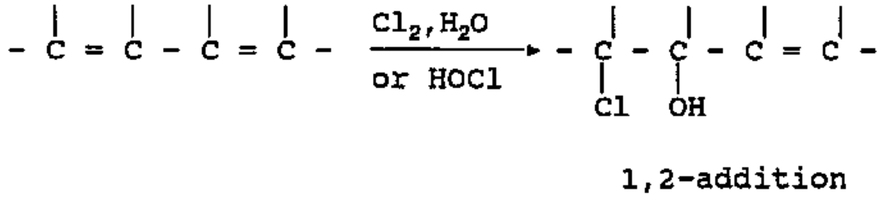
In additions to conjugated double bonds, the electrophilic reagent may attach itself not only to a pair of adjacent carbons (1,2-addition), but also to the carbons at the two ends of the conjugated system (e.g., 1,4 - addition in the case of conjugated dienes). This is shown in the following equation (3) for the addition of Cl_2 to a conjugated diene.



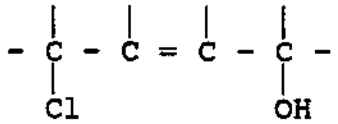
(3)

Since addition of chlorine to double bonds is expected to increase the hydrophobic character of the membranes, chlorination of the dehydrated PVAL does not explain the significant increases in water flux that occurred after chlorine shock-treatment of Membranes LP-1 to LP- 8. Furthermore, chlorination of double bonds is usually carried out in an inert solvent such as carbon tetrachloride.

In aqueous solution, the reaction between Cl_2 and H_2O results in the *in situ* formation of hypochlorous acid, HOCl (eqn. (1)). Therefore, in the present study it seems more likely that the addition of Cl_2 in the presence of H_2O will involve the addition of the elements of hypochlorous acid, namely HO- and -Cl [54]. If 1,2-addition occurs, as shown in eqn. (4) for a conjugated diene, this reaction yields compounds containing chlorine and hydroxyl groups on adjacent carbons, i.e. chlorohydrins. Obviously, an increase in the length of the conjugated double-bond sequences will also increase the number of possible addition products.



and



$$-\underset{\mathrm{Cl}}{\underset{|}{\overset{|}{C}}}-\overset{|}{C}=\overset{|}{C}-\underset{\mathrm{OH}}{\underset{|}{\overset{|}{C}}}-$$

(4)

1,4-addition

The addition of both chlorine and hydroxyl groups to the double bonds of dehydrated PVAL seems to offer the best explanation for the fact that the increase in permeate flux after chlorine treatment was not accompanied by a significant decrease in salt retention. However, the mechanism of interaction of hypochlorous acid with dehydrated PVAL needs to be investigated in considerably more detail before any definite conclusions can be reached. Other reactions, such as hydration (addition of H_2O to double bond) and hydroxylation (addition of two hydroxyl groups to double bond), could also result in an increase in water permeability, but this will certainly be accompanied by a loss of salt-retention capability.

2.3.1.3 Conclusions

(a) Both flat-sheet and tubular composite membranes could be prepared by depositing aqueous PVAL solutions on asymmetric porous PES substrate membranes. The PVAL coatings were insolubilized by dehydration during heat treatment in the presence of H_2SO_4 as catalyst. Elimination of water during heat treatment resulted in discolouration of the membranes due to formation of conjugated unsaturation.

(b) The influence of several variables on the RO performance of PES-PVAL composite membranes was investigated. It was found that heat-treatment temperature and H_2SO_4 concentration played the most significant roles in determining the extent of dehydration and, consequently, flux and salt-retention properties. The results of this investigation showed that a simple manipulation of one or two variables could lead to gel-layer membranes with widely differing salt-retention and water permeability characteristics.

(c) While shock-treatment of the membranes with chlorine apparently had no detrimental effect on salt-retention capability, it resulted in a considerable increase in permeate flux. This could possibly be attributed to the interaction of hypochlorous acid with the double bonds of dehydrated PVAL, resulting in addition of both chlorine and hydroxyl groups.

(d) For the flat-sheet PES-PVAL gel-layer membrane system, NaCl retentions (tested on a 2000 mg/l NaCl feed) of 70 - 85% and permeate fluxes of 700 - 800 lmd could be achieved at 2 MPa, while $MgSO_4$ retentions (tested on a 500 mg/l $MgSO_4$ feed) of > 90%, with accompanying fluxes of about 600 lmd, could be obtained at 2 MPa.

(e) The promising RO performances obtained at 2 MPa indicated that the PES - PVAL gel-layer membrane system could function as medium-retention, medium-flux RO membranes at relatively low operating pressures, even in the absence of an additional interfacially formed salt-retention barrier. However, an improvement of salt-retention and water permeability characteristics by further chemical modification of partially dehydrated PVAL remained desirable.

(f) Double bonds introduced during acid-catalyzed dehydration provide convenient sites for chemical modification by, for example, electrophilic addition, free-radical addition and cycloaddition reactions. These possibilities are presently being investigated and will be mentioned in section 2.3.4.

(g) For desalination of brackish water and industrial wastewater, a thin salt-retention barrier will ultimately be formed on the PVAL gel layer by interfacial polycondensation. In this case, the insolubilized PVAL coating alone is not required to exhibit high salt-retention capabilities. Consequently, coating solution compositions and fabrication conditions can be adjusted to give low-retention, high-flux gel layers. For this purpose, the use of low catalyst concentrations and curing temperatures ≤ 100°C will be advisable.

2.3.2 INSOLUBILIZATION BY CROSSLINKING WITH POLY(METHYL VINYL ETHER-*alt*-MALEIC ANHYDRIDE)

2.3.2.1 Background

A reasonably comprehensive review of the literature pertaining to the development of PVAL-based membranes, as well as a discussion of common ways of insolubilizing PVAL, has been presented in section 2.2.

Examples of the use of polymer blends as membrane materials can be found in the work of Cadotte et al. [55] and Hopfenberg et al. [56]. The preparation of interpolymer anionic composite membranes, using PVAL as membrane matrix and poly(styrene sulphonic acid) [PSSA] as polyelectrolyte, was reported by Koyama et al. [57-59]. Gryte and Gregor [60, 61] reported the preparation and characterization of interpolymer membranes based on a hydrophobic matrix polymer, namely, poly(vinylidene fluoride). Both anionic and cationic fixed charge groups were incorporated into the films by employing the appropriate polyelectrolytes.

Gryte [62] prepared interpolymer membranes from PVAL and poly(styrene sodium sulphonate) [PSSNa], using 1,1,1-tris(hydroxymethyl)propane as crosslinking agent. Interpolymer ion exchange membranes were prepared from a blend of three hydrophilic polymers, namely, PVAL (membrane matrix), PSSNa (polyelectrolyte), and poly(methyl vinyl ether-*alt*-maleic anhydride) [MVE-*alt*-MAH] as crosslinking agent [63]. This system differs from polyelectrolyte complex membranes developed by Michaels [64], wherein the gel network resulted from an ionic coacervation of the two oppositely charged polymeric components.

In section 2.3.1 we reported on the formation of insoluble hydrophilic PVAL gel layers by acid-catalyzed dehydration of PVAL. In this section, gel-layer membranes were prepared from aqueous compatible blends of PVAL and MVE-*alt*-MAH. Homogeneity is a prime criterion for membrane strength and selectivity. It has been shown [63] that aqueous solutions of PVAL and MVE-*alt*-MAH are highly compatible and that this compatibility is temperature-independent. Therefore, phase separation is not a problem in this particular two-component system.

Since both PVAL and MVE-*alt*-MAH are hydrophilic and water-soluble, crosslinking of the chains into a three-dimensional network is essential to maintain the integrity of the membranes in an aqueous environment. In this study, crosslinked gel-layer membranes were formed by heating the polymer blend coatings at temperatures $\geq$ 125°C.

2.3.2.2 Materials and Methods

Chemicals

Partially hydrolyzed grades of PVAL (degree of hydrolysis 86 - 89%) were used for the formation of hydrophilic gel sub-layers. PVAL of average molecular mass 72 000 and 125 000 were used. Poly(methyl vinyl ether-*alt*-maleic anhydride) [GANTREZ AN-149, a product of GAF CORPORATION] was used as polyfunctional crosslinking agent. Poly(arylether sulphone) [VICTREX 4800G, a product of ICI, England] was used for the manufacture of asymmetric substrate membranes. Concentrated H_2SO_4 (98%) was used as esterification catalyst in some experimental trials. Reverse osmosis properties of crosslinked gel layers were determined using sodium chloride (CP grade) feed solutions.

Membrane Fabrication

Flat-sheet asymmetric substrate membranes were again prepared by the phase-inversion deposition of poly(arylether sulphone) [PES] on a non-woven fabric [Viledon™; Carl-Freudenberg, Germany]. PES substrate membranes were stored in distilled water to avoid drying and cracking.

Blends of PVAL and MVE-*alt*-MAH were dissolved in distilled water by continuous stirring at room temperature for a period of 24 hrs. Membrane coating solutions were filtered before use to remove any undissolved matter. Flat-sheet composite membranes were prepared by depositing PVAL/MVE-*alt*-MAH blend solutions on asymmetric PES substrates, using the dip-coating technique. Typically, the substrate was drained of excess water, immersed in the PVAL/MVE-*alt*-MAH blend solution, removed and drained of excess coating solution.

Membrane coatings were then crosslinked by heat treatment at a given temperature for a certain period of time. The coating solution compositions and membrane fabrication conditions are summarized in Table 15.

TABLE 15:

Compositions of coating solutions and fabrication conditions of PVAL/MVE-*alt*-MAH membranes

Solution No.	1	2	3	4	5	6
PVAL (MM 72 000)[a] (mass %)	1.0	1.0	-	2.0	1.0	-
PVAL (MM 125 000)[b] (mass %)	-	-	-	-	-	1.0
MVE-alt-MAH[c] (mass %)	1.0	1.0	2.0	1.0	2.0	1.0
Concentrated H_2SO_4 (mass %) -	0.5	-	-	-	-	
<u>Fabrication condtions</u>:						
Support predrain time (min)	5	5	5	5	5	5
Wetting time (min)	10	10	10	10	10	10
Draining time (min)	8	8	5	5	5	5
Curing time (min)	20	20	20	20	20	20
Curing temp. (°C)	125	125	125	125	125	125

a. SAARCHEM; 86 - 89% hydrolyzed.
b. BDH; 86 - 89% hydrolyzed.
c. Gantrez AN-149: GAF CORPORATION.

Evaluation of Membrane Performance

The membrane evaluation equipment has been presented earlier in Fig. 2. Membrane compositions and testing conditions for the individual experiments are indicated in the tables and figures presented in the RESULTS AND DISCUSSION section 2.3.2.3. Typically, the RO properties of the membranes were tested at 20°C and 2 MPa on a 2000 mg/l NaCl feed solution. The membranes were evaluated at different pH values of the feed solution (i.e., pH 3, pH 7 and pH 11). The pH of the feed solution was adjusted by adding 8% (m/v) HCl or 10% (m/v) NaOH solutions. The salt-retention and flux values have been defined earlier (section 2.3.1.2).

2.3.2.3 Results and Discussion

Mechanism of Insolubilization of PVAL/MVE-*alt*-MAH Blend Membranes

When MVE-*alt*-MAH is dissolved in water, it hydrolyzes to form maleic acid residues in the repeating unit. In the PVAL/MVE-*alt*-MAH system, the gel network is caused by the formation of interchain ester linkages between the hydroxyl groups of PVAL and the carboxyl groups of hydrolyzed MVE-*alt*-MAH. In fact, each of these two polymers acts as a crosslinking agent for the other. In membranes made from this system, electrolyte retention occurs by an ion exclusion mechanism, which is caused by the fixed charges of the carboxylate groups. The use of a polyfunctional polycarboxylic acid (i.e., hydrolyzed MVE-*alt*-MAH) in this work, therefore serves two purposes: to provide effective crosslinking and, simultaneously to impart a fixed charge character to the crosslinked membranes. The charge character results from the presence of carboxylate groups of the hydrolyzed but unesterified MVE-*alt*-MAH.

Reverse Osmosis Performance

The effect of different ratios of PVAL : MVE-*alt*-MAH on membrane performance were evaluated during this study. The effect of curing temperature, curing time and heat treatment in the absence or presence of an acid catalyst (H_2SO_4) on RO performance were also investigated. The compositions of coating solutions were as given in Table 15 (see section 2.3.2.1).

The salt-retention and flux properties of membranes prepared from Solutions 1 and 2 varied with the pH of the feed solution, as shown in Figs. 6 and 7.

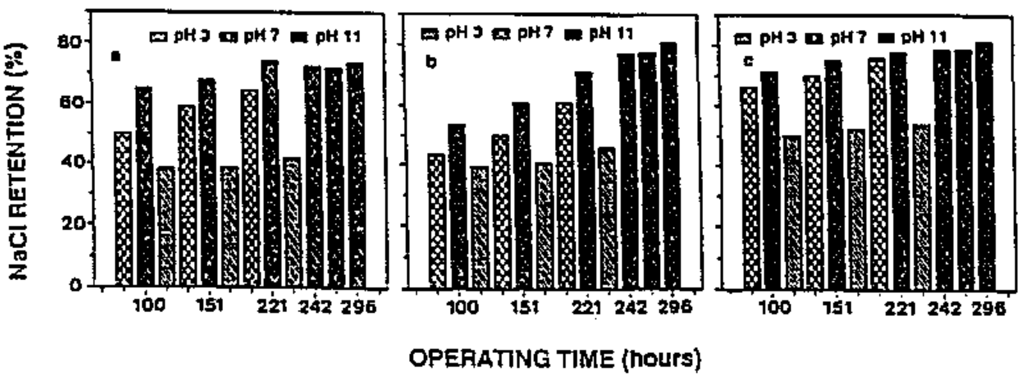


FIGURE 6:

Variation of NaCl retention with the pH of the feed solution during three pH cycles: Trial 1. (a) Membrane 1: Solution 1 cured at 125°C. (b) Membrane 2: Solution 1 cured at 130 - 135°C and (c) Membrane 3: Solution 2 cured at 125°C. Tested at 20°C and 2 MPa on a 2 000 mg/l NaCl feed.

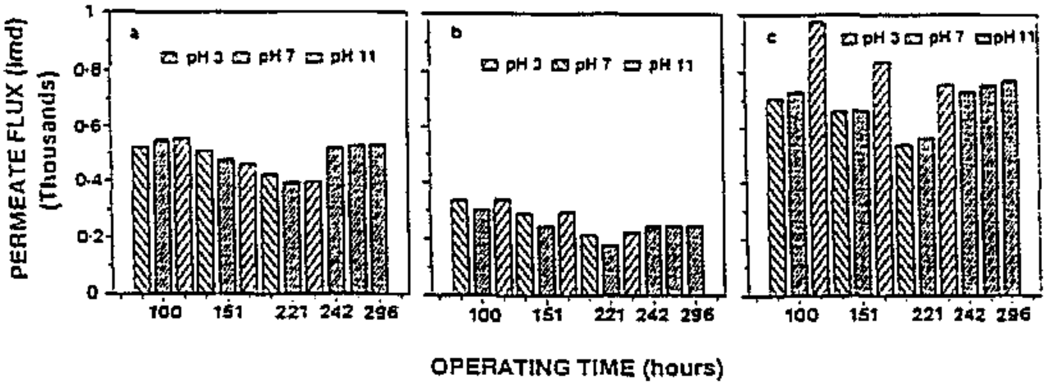


FIGURE 7:

Variation of permeate flux with the pH of the feed solution during three pH cycles: Trial 1. (a) Membrane 1: Solution 1 cured at 125°C. (b) Membrane 2: Solution 1 cured at 130 - 135°C and (c) Membrane 3: Solution 2 cured at 125°C. Tested at 20°C and 2 MPa on a 2 000 mg/l NaCl feed.

All membranes exhibited the highest retentions at pH 11, while the lowest retentions were measured at pH 3. In general, the same trend was observed at all pH values, namely, an increase in salt retention with increasing operating time. The membrane which was cured in the presence of H_2SO_4 catalyst (Fig. 6c) exhibited the highest salt-retention capability at all pH values of the feed solution.

The fluxes of these membranes at different pH values showed a complex behaviour (Fig. 7). Permeate flux decreased with increasing operating time (i.e., after each cycle of pH 7 $\longrightarrow$ pH 11 $\longrightarrow$ pH 3) at all pH values. For all three membranes shown in Fig. 7, the highest fluxes were generally obtained at pH 3. A comparison of Figs. 7a and 7b shows that a higher curing temperature resulted in a considerable decrease in permeate flux. One would expect this sharp decline in flux to be attributable to a higher degree of crosslinking, but it is difficult to imagine that a temperature increase of 5 - 10°C could make such a big difference. Furthermore, the flux decline was not accompanied by higher salt-retention capability.

It was not advisable to use curing temperatures above 125°C, due to the possible detrimental effect that prolonged heat treatment at high temperatures could have on the asymmetric porous structure of the PES substrate membrane. It is possible that heat treatment of the PES substrate in the presence of water (i.e., the aqueous coating solution) could cause a plasticizing effect, resulting in sealing of some of the finer pores at the substrate surface. This, in turn, could result in a decrease in water permeability. In view of this possibility, and since curing temperatures of less than 125°C would probably be too low to facilitate ester-bond formation, it was decided to select a curing temperature of 125°C for all subsequent membrane preparations.

The most significant finding in this experimental trial was the fact that curing of a membrane at 125°C in the presence of H_2SO_4 catalyst resulted not only in higher salt retentions than those exhibited by membranes cured in the absence of catalyst, but also in considerable increases in permeate flux.

After the membranes have been subjected to three cycles of pH 7 $\longrightarrow$ pH 11 $\longrightarrow$ pH 3, they were allowed to equilibrate at pH 11 during the last 72 hrs of the test. The RO performances at pH 11 (recorded over a period of approximately 200 hrs) are shown in Table 16.

TABLE 16:

Variation of RO properties of PVA/MVE-*alt*-MAH membranes with the pH of the feed solution during three separate trials

Observed Trends	TRIAL 1		TRIAL 2		TRIAL 3	
	No Catalyst[1]	Catalyst[2]	No Catalyst[1]	Catalyst[2]	No Catalyst[1]	Catalyst[2]
Highest NaCl retention	pH 11	pH 11	pH 11	pH 11	pH 11	pH 11
Lowest NaCl retention	pH 3	pH 3	pH 3	pH 3	pH 3	pH 3
Retention behaviour after three pH cycles	Increased	Increased	Decreased	Decreased	Decreased	Decreased
Highest flux	pH 7	pH 3	pH 7	pH 3	pH 7	pH 11
Lowest flux	pH 3	pH 7	pH 3	pH 11	pH 3	pH 3
Flux behaviour after three pH cycles	Decreased	Decreased	Decreased	Increased	Decreased	Decreased
Average NaCl retention at pH 3 after three cycles	39,8%	52,4%	26.1%	32.6%	24,0%	24,9%
Average NaCl retention at pH 7 after three cycles	57,9%	70,9%	49.2%	53.5%	47,0%	50,2%
Average NaCl retention at pH 11 after three cycles	69,1%	74,7%	51,4%	56,4%	56.3%	64,5%
Average flux at pH 3 after three cycles	468 lmd	855 lmd	620 lmd	1423 lmd	284 lmd	631 lmd
Average flux at pH 7 after three cycles	483 lmd	634 lmd	769 lmd	907 lmd	423 lmd	781 lmd
Average flux at pH 11 after three cycles	472 lmd	653 lmd	632 lmd	624 lmd	360 lmd	820 lmd

[1] Solution 1

[2] Solution 2

Figure 8 shows the fluctuation of salt retention and flux due to successive pH variations.

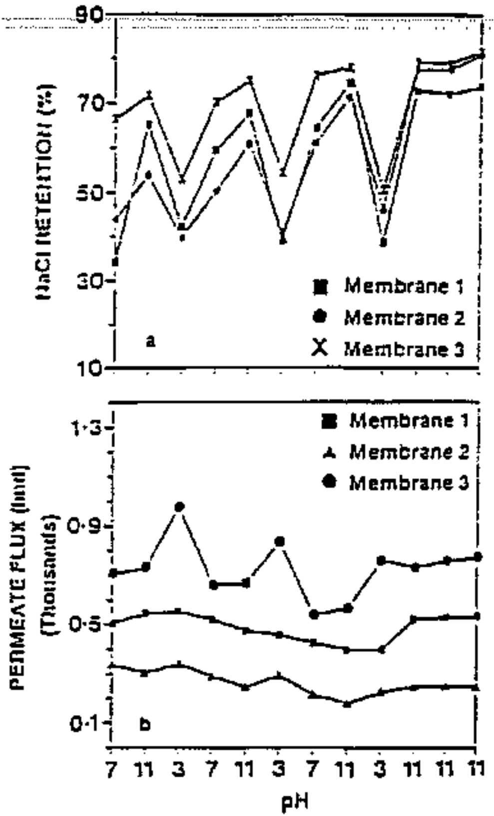


FIGURE 8:
Fluctuation of salt retention (a) and permeate flux (b) due to successive pH changes.
Membrane 1: Solution 1 cured at 125°C, Membrane 2: Solution 1 cured at 130 - 135°C and
Membrane 3: Solution 2 cured at 125°C. Tested at 20°C and 2 MPa on a 2 000 mg/l NaCl feed.

The flux and salt-retention properties had apparently stabilized at pH 11 after a total operating time of 296 hrs. During this period the salt-retention capability of Membranes 1 and 2 increased, while the flux decreased slightly. In the case of Membrane 3, both the salt retention and the flux increased moderately.

In an attempt to reproduce the results of this first trial, two further trials were conducted with membranes prepared from Solution 1 (no catalyst) and Solution 2 (catalyst). The fabrication conditions were as described earlier.

Four membranes were prepared from each coating solution and all membranes were subjected to three pH cycles (pH 7 ——▸ pH 11 ——▸ pH 3). For comparison, the trends observed during these three trials are also summarized in Table 16. It is obvious that the results obtained in the first trial could not be reproduced in subsequent trials, regardless of the fact that the same coating solutions and fabrication conditions were employed. The following aspects of this study deserved further discussion and which is to be found in the publication entitled: Poly(vinylalcohol) gel sub-layers for reverse osmosis membranes. II. Insolubilization by crosslinking with poly(methyl vinyl-*alt*-maleic anhydride, Addendum 1.

(a) pH-Dependence of RO performance;

(b) The role of H_2SO_4 in the reaction and the differences between the RO properties of membranes cured in the absence or presence of H_2SO_4;

(c) Reproducibility of salt-retention and flux characteristics;

(d) Hydrolytic stability of the crosslinked gel-layer membranes.

2.3.2.4 Conclusions

(1) Composite PES-PVAL gel-layer membranes could be formed by depositing aqueous compatible blends of PVAL and MVE-*alt*-MAH on flat-sheet asymmetric PES substrate membranes. Insolubilization occurred by the formation of interchain ester crosslinks during heat treatment. The crosslinked PVAL gel-layer membranes appeared to be stable in aqueous environments.

(2) All membranes exhibited some level of NaCl retention, as well as relatively low water permeabilities, when cured at 125°C for 20 min, indicating that crosslinking did occur in all cases. NaCl retentions > 60% and permeate fluxes of 600 - 900 lmd could be achieved at pH 11 when membranes were tested at 2 MPa on a 2000 mg/l NaCl feed.

(3) The fixed charge character of crosslinked PVAL membranes, caused by the presence of carboxyl groups of hydrolyzed but unesterified MVE-*alt*-MAH, resulted in a variation of salt-retention and water permeability characteristics with the pH of the feed solution. The pH-dependence of RO performance was attributed to the different degrees of ionization of the first and second maleic acid carboxyl groups at different pH values.

(4) Membranes were subjected to several cycles of pH 7 ⟶ pH 11 ⟶ pH 3 in three separate trials. The pH-dependence of RO properties, as well as the levels of salt retention and permeate flux, differed during these three trials. Possible reasons for the lack of reproducibility of RO performance were discussed.

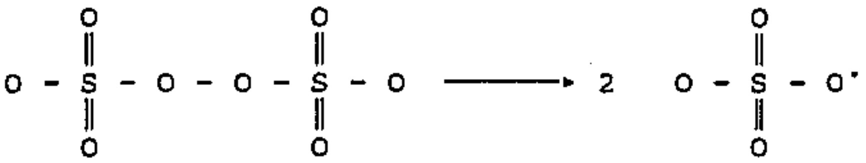
(5) The effect of H_2SO_4 as esterification catalyst was studied. Membranes that were heat-cured in the presence of H_2SO_4 catalyst exhibited higher salt-retention capabilities and much higher fluxes than membranes cured in the absence of catalyst. The results suggested that H_2SO_4 was not only a catalyst, but also a reactant. This possibility is presently being investigated.

(6) Different ratios of PVAL : MVE-*alt*-MAH were evaluated in this study. Membranes prepared from solutions containing 1% PVAL, 1% MVE-*alt*-MAH and 0.5% H_2SO_4 catalyst (i.e., a PVAL : MVE-*alt*-MAH molar ratio of 3.5 : 1) exhibited sufficiently high permeate fluxes for application as gel sub-layers for RO membranes.

2.3.3 INSOLUBILIZATION BY CROSSLINKING WITH POTASSIUM PEROXYDISULPHATE

2.3.3.1 Background

Peroxydisulphates (the trivial name "persulphate" is also commonly used) have been widely used, either alone or in various redox combinations, as initiators of aqueous vinyl polymerizations. With peroxydisulphate alone as the initiator, the primary initiating radicals are sulphate ion radicals generated by its thermal or photochemical decomposition:



$$O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O \longrightarrow 2\quad O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O^{\bullet}$$

Apart from being a free-radical source, the peroxydisulphate ion is also one of the strongest oxidizing agents known in aqueous solutions. The oxidation of low molecular mass alcohols by peroxydisulphate has been studied extensively [65-72]. These studies have elucidated that peroxydisulphate is reduced to sulphate ion in the presence of alcohols, from which aldehydes and ketones are produced upon oxidation, depending on whether the starting alcohol is primary or secondary, respectively. These reactions have been reviewed by House [73].

Similarly, the hydroxyl groups of PVAL have been found to be oxidized to ketones by peroxydisulphate [74]. In addition, grafting took place when peroxydisulphate was used as a catalyst to initiate the graft polymerization of monomers such as methyl methacrylate [74], maleic anhydride [75, 76] and acrylonitrile [76] onto PVAL. This suggested that peroxydisulphate was able to generate free radicals on the PVAL chain. The reaction of peroxydisulphate with PVAL has been used to prepare mechanically stable crosslinked gels for packaging materials. In the study reported here, peroxydisulphate was used as a free-radical source for the crosslinking of PVAL to form hydrophilic gel sub-layers for RO membranes.

2.3.3.2 Materials and Methods

Chemicals

Poly(arylether sulphone) [VICTREX 4800G, a product of ICI, England] was used for the formation of asymmetric substrate membranes. Both partially-hydrolyzed and fully-hydrolyzed grades of PVAL were used for the preparation of hydrophilic gel sub-layers. PVAL of molecular mass 72 000 (degree of hydrolysis 86 - 89 mol %) and 115 000 (degree of hydrolysis 100 mol %) were purchased from SAARCHEM and ALDRICH, respectively. Potassium peroxydisulphate, $K_2S_2O_8$, (CP grade; 98%) was obtained from FLUKA. The RO performances of crosslinked PVAL membranes were determined using NaCl, hydrated $MgSO_4$ and $CaSO_4$ (CP grades) feed solutions.

Preparation of PVAL/$K_2S_2O_8$ solutions

The large-scale preparation of aqueous solutions of PVAL involving the use of steam-heated or jacketed stainless steel mixers. To prepare solutions on a smaller scale without the use of specialized equipment, the method described below has been found to be the most effective and was used throughout.

The calculated amount of distilled water was stirred vigorously in a Schott bottle with a magnetic heater/stirrer plate and a large magnetic follower. The PVAL was then weighed off and slowly added to the stirred water, whereafter the temperature of the mixture was increased to above 90°C. When the solvation was complete, the solution was cooled to room temperature, potassium persulphate was introduced and the mixture stirred (without heating) until a clear solution was obtained. The solution was then filtered through a Buchner funnel to remove any impurities and other undissolved matter.

Membrane fabrication

Tubular (13 mm diameter) and flat-sheet substrate membranes were manufactured by the phase-inversion deposition of poly(arylether sulphone) [PES] on a polyester non-woeven fabric [Viledon™: Carl-Freudenberg, Germany]. Tubular asymmetric substrate membranes were either obtained from MEMBRATEK (Code 719 membranes) or manufactured in-house from identical casting solutions, (IPS Code 546T membranes).

PVAL membranes were prepared by the deposition of the PVAL/$K_2S_2O_8$ solution onto the support membrane in a process referred to as dip-coating. In this process the support tubes were first drained of water and then immersed or dipped into the aqueous solution of PVAL and $K_2S_2O_8$ contained in a cylindrical glass tube. The dimensions of the glass tube (diameter, 50 mm; length, 600 mm) permitted the coating of six membranes simultaneously. After their removal from the solution, the membranes were again drained to remove excess solution and subsequently heated in a specially designed vertical draft oven to effect the crosslinking of the PVAL film.

A phenomenon termed "solution maturation", involving reactions occurring in the PVAL/$K_2S_2O_8$ solution before membrane fabrication, was also found to be an important variable in the production process. Some solution were therefore deliberately matured for extended periods, and membranes were made from them at various stages of the maturation process.

In one attempt to produce membranes with higher permeate fluxes, the UF support membranes were treated with glycerol before the deposition of the PVAL membrane. The effect of different grades of PVAL on membrane performance was also studied in the above experiment.

Membrane evaluation

Details pertaining to membrane evaluation are described in section 2.3.1.2

2.3.3.3 Results and Discussion

Mechanism of insolubilization of PVAL

The mechanism of insolubilization of PVAL with peroxydisulphate has been discussed at length in the publication: Poly(vinylalcohol) gel sub-layers for reverse osmosis membranes. III. Insolubilization by crosslinking with potassium peroxydisulphate. (See Addendum 1.)

Parameters influencing membrane performance and RO Performances of PVAL $K_2S_2O_8$ (PK) composite membranes.

Extensive studies were carried out into the parameters influencing the RO performance of the PVAL-$K_2S_2O_8$ (PK) membranes. While a comprehensive summary of results will be presented here, full details are to be found in the abovementioned publication (see Addendum 1), and in a copy of a M.Sc.-thesis: Polyvinylalcohol and amine-modified polyvinylalcohol nanofiltration and reverse osmosis membranes, by Deon Bezuidenhout [45].

Following from the methods used in the preparation of these membranes, it is obvious that some or all of the following variables may influence their salt-retention properties:

(i) PVAL concentration
(ii) Support pre-drain time
(iii) $K_2S_2O_8$ concentration
(iv) PVAL/$K_2S_2O_8$ dip time
(v) PVAL/$K_2S_2O_8$ drain time
(vi) Curing temperature
(vii) Curing time

Unless it is otherwise indicated, all references to the use of PVAL in the procedures for membrane fabrication are to the grade PVAL-B (MM=72000; DH=88%). The effect of using another grade of PVAL, as well as the effect of solution maturation and glycerol pre-treatment were, however, also investigated in experiments designed specifically for the purpose. The list of variables may therefore be completed by the addition of the following:

(viii) PVAL molecular mass
(ix) PVAL degree of hydrolysis
(x) Maturation time
(xi) Maturation temperature
(xii) Pre-treatment conditions

The conditions used for the fabrication of the PK membranes were as listed in Table 17, except where it is indicated that one or more of the conditions were altered.

TABLE 17:
Basic conditions adhered to in the production of PK membranes

PARAMETER	VALUE	
Pre-drain	2	min
[PVAL]	3	%
[$K_2S_2O_8$]	1.5	%
Dip time	2	min
Drain time	5	min
Curing time	20	min
Curing temperature	80	°C

(a) Effect of PVAL concentration

PES supports (546 T) were coated with solutions of PVAL ranging from 0,5 to 3,0 % to determine the effect of PVAL concentration on the salt-retention properties of the PK and PVAL membranes. Potassium persulphate was added at a PVAL : $K_2S_2O_8$ ratio of 3 : 1 to ensure equal crosslink densities. An uncoated support membrane was used as a control. Four membranes were made from each PVAL solution (0,5%, 1,0%, 1,5%, 2,0%, 3,0%) and were used as follows:

- Two of each for salt-retention and permeate flux evaluation;
- Two of each for evaluation after further treatment with PIP and IPC.

Figures 9 and 10 show the effect of the PVAL concentration on the water flux and salt-retention, respectively. The legend symbols refer to different operating pressures.

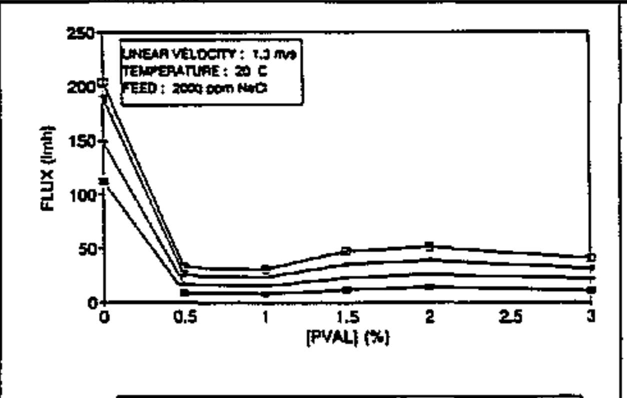


Figure 9:
Effect of PVAL concentration on permeate flux
at different pressures.

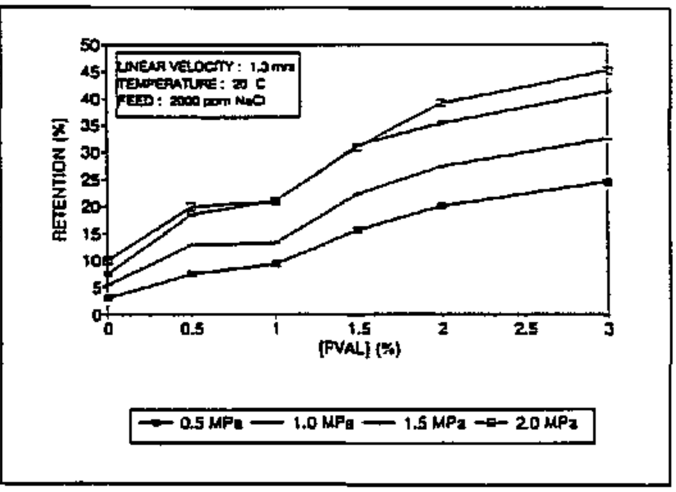
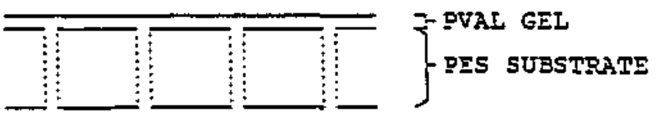


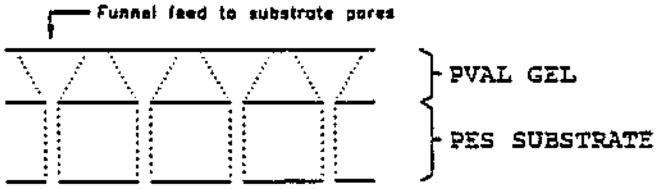
Figure 10:
Effect of PVAL concentration on NaCl retention
at different pressures.

It is evident that an increase in the PVAL concentration results in an appreciable increase in retention (retention at 3% PVAL is approximately twice as high as that at 0,5% PVAL). It is known that the retention of a membrane is defined by its chemical structure and not by its thickness. Yet it is obvious that higher concentrations of PVAL in the coating solution leads to a thicker layer. The premise is, therefore, that the PES membrane has pores of variable sizes, and that a thicker gel-layer seals imperfections caused by larger pores.

Figure 9 does not show the expected decrease in permeate flux as the PVAL concentration, and thus the membrane thickness, increases. It must be remembered that a PES membrane has only about 2% of its surface covered by pores. If it is accepted that the 0.5% gives a thin coating, then the situation arises as is sketched below:



With a thin coating not all of the coating is active, as much of it lies over a non-porous area of the substrate. When the coating is thicker, as with the use of a more concentrated PVAL solution, then the following sketch would be more applicable:



The thicker layer is sometimes referred to as a bucket layer, as it channels water to the pores in the substrate.

The effect of pressure on membrane properties, is shown in Figures 11 and 12. These represent the same data as the previous two figures (9 and 10), but here the flux and retention are plotted against pressure, with the legends referring to the various PVAL concentrations.

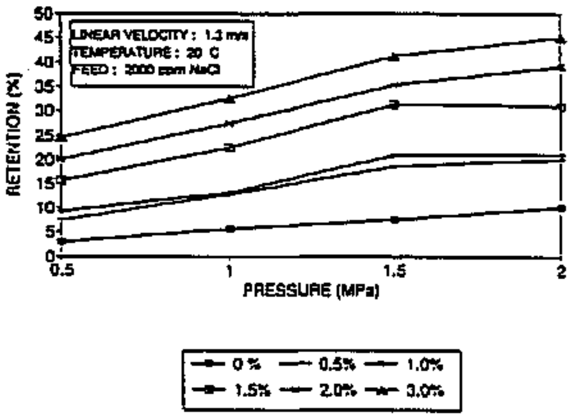


Figure 11:
Effect of pressure on permeate flux at
different PVAL concentrations
(1st experiment)

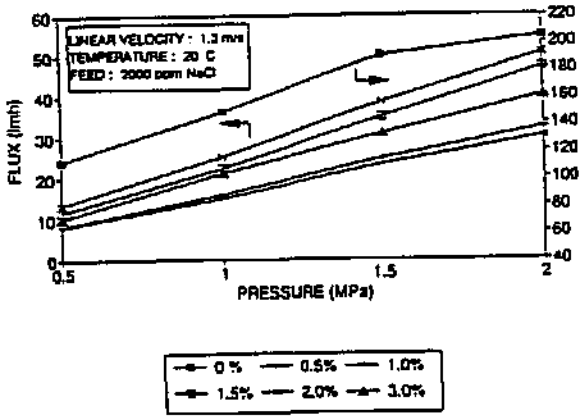


Figure 12:
Effect of pressure on NaCl retention at
different PVAL concentrations
(1st experiment)

As in the solution-diffusion model, the flux of the PK membranes increases linearly with increase in pressure, whereas the retention increases asymptotically toward an upper limit.

(b) Effect of support pre-drain time

Since the support membranes are stored in water, it is neccessary to drain them prior to dip-coating to ensure that there is no excess water which could lead to dilution of the PVAL/$K_2S_2O_8$ solutions. A time of 2 min was found to be ample for the drainage of the excess water from the support membranes.

(c) Effect of $K_2S_2O_8$ concentration

Membranes made from 3% PVAL-B solutions containing various amounts of $K_2S_2O_8$ were evaluated before and after treatment with PIP and IPC to determine the effect of the $K_2S_2O_8$ concentration on their properties. The $K_2S_2O_8$ was dissolved in the PVAL solutions only after the latter had cooled to room temperature, to prevent premature crosslinking at high temperatures. Because one persulphate ion can produce two ion radicals, the minimum number of monomer units between crosslinks (for 3% PVAL-B) is shown in Table 18.

TABLE 18:

Crosslink density of PK membranes

$[K_2S_2O_8]$ %	UNITS/CROSSLINK
0,1	46
0,25	37
0,5	18
1,0	9.0
1,5	6.8
2,0	4,6

Figures 13 and 14 show flux and retention of PK membranes vs. $K_2S_2O_8$ concentration, respectively, at operating pressures ranging from 0,5 to 2,0 MPa.

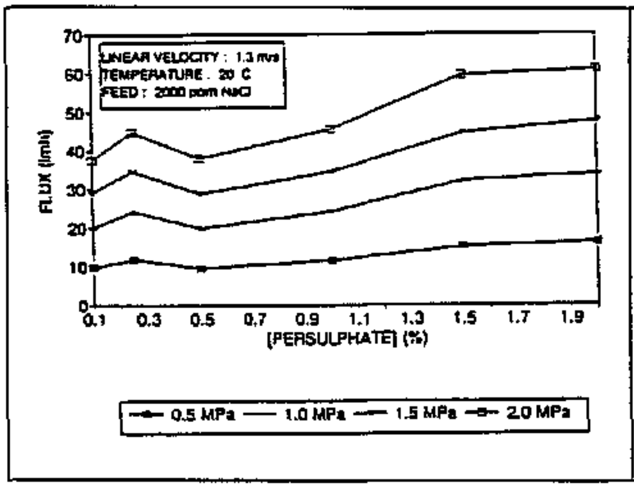


Figure 13:
Effect of persulphate concentration on permeate flux at different pressures
(2nd experiment)

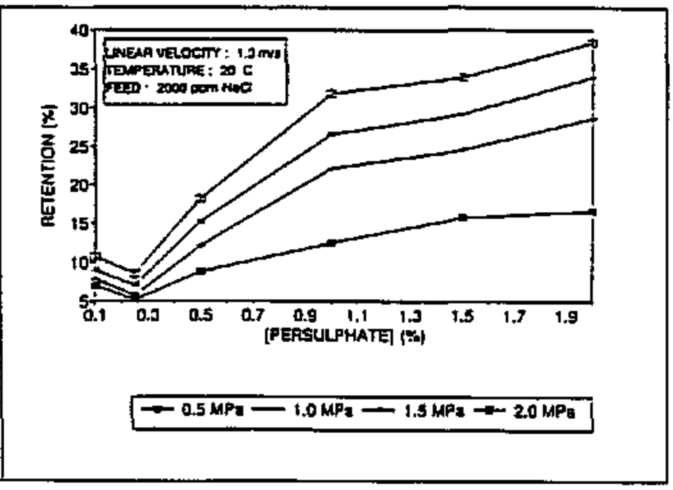
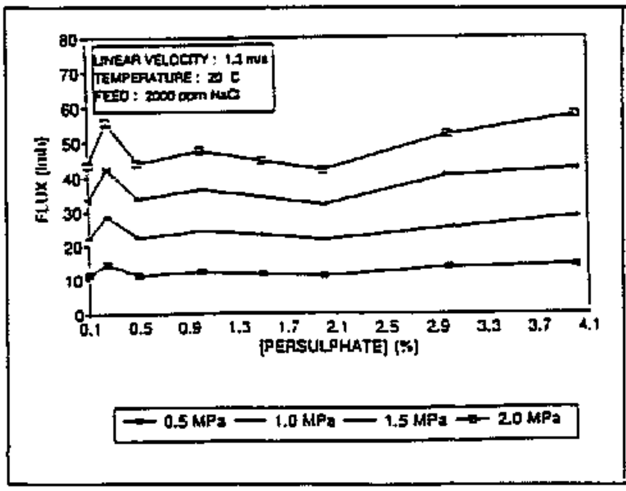


Figure 14:
Effect of persulphate concentration on NaCl retention at different pressures
(2nd experiment)

As expected, the retention increased with increase in $K_2S_2O_8$ and thus with crosslink density of the membrane. The flux also showed an unexpected increase with increase in $K_2S_2O_8$. An explanation herefore could be that the membranes made with very low $K_2S_2O_8$ concentrations were too lightly crosslinked, and that the PVAL gel was broken up and washed into the support structure, resulting in fouling of the membrane and low fluxes.

This experiment was repeated to determine its reproducibility and to try to explain the irregularities present in Figures 13 and 14. The same $K_2S_2O_8$ concentrations with the addition of two added concentrations (3% and 4%), were used. Figures 15 and 16 show the NaCl retention properties of these membranes 22 h after start-up.



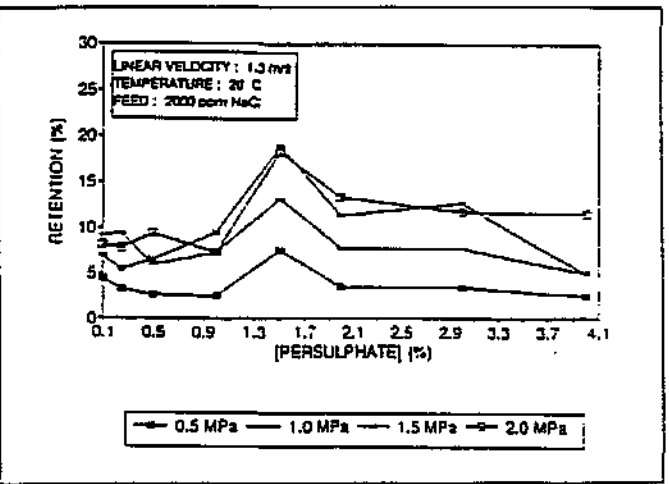


Figure 15
Effect of persulphate concentration on permeate flux at different pressures

Figure 16
Effect of persulphate concentration on NaCl retention at different pressures

Figure 16 shows the retention of salt to be much higher at the concentration of [$K_2S_2O_8$] of 1,5% than at any other concentration and it was later discovered that this was due to the effect of ageing or maturation of the PVAL/$K_2S_2O_8$ solutions. The 1,5% $K_2S_2O_8$ solution was prepared a few days before the other solutions were, and this resulted in the higher retention. The marked effect of solution maturation on membrane properties will be discussed in detail in section f.

(d) Effect of PVAL dip and drain times

The support membranes (stored in a waterbath to prevent drying) were pre-drained for 2 min to remove excess water and then dipped into a glass tube containing the PVAL/$K_2S_2O_8$ solution for 5 min, after which the support was drained of excess PVAL/K2S2O8 solution for 2 min. The dip time of 5 min was considered to be sufficient to achieve uniform wetting of the PES supports, and the variation of this variable (within reasonable limits) was found to have little effect on the membrane properties.

(e) Effect of curing time and temperature

Membranes made from the two solutions listed in Table 11 were cured at 60°C and 80°C for various times to determine their effect on the membrane properties. Higher temperatures were not used because of the possible detrimental effect on the PES supports.

TABLE 19:

Solutions used to determine the effect of curing time and temperature on the performance of PVAL/$K_2S_2O_8$ membranes

	SOLUTION 1	SOLUTION 2
[PVAL-B] (%)	2.0	3.0
[$K_2S_2O_8$] (%)	0.5	1.0
[H_2O]	97.5	96.0

(a) Curing at 80°C

Figures 17 and 18 show the flux and NaCl retention of the membranes made from Solution 1 plotted against curing time at 80 °C. The lowest flux is obtained with a curing time of 5 min and the highest with a time of 15 min, the difference between the two values being approximately 100%. The NaCl retention did not show such a significant dependence on the curing time. In this case no increase in retention was expected as the curing time was increased.

For membranes made from solution 2, the flux decreased (Figure 19) and the retention increased significantly with an increase in curing time at 80 °C, the largest increase in retention being between the curing times of 15 and 20 min (Figure 20).

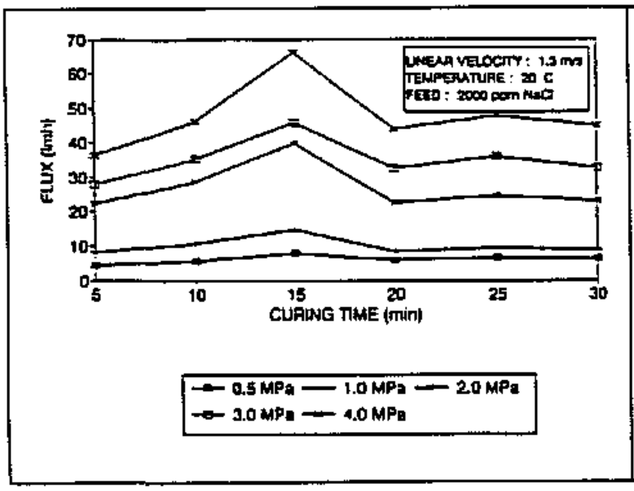


Figure 17:
Effect of curing time on permeate flux at different pressures. (Solution 1 at 80 °C)

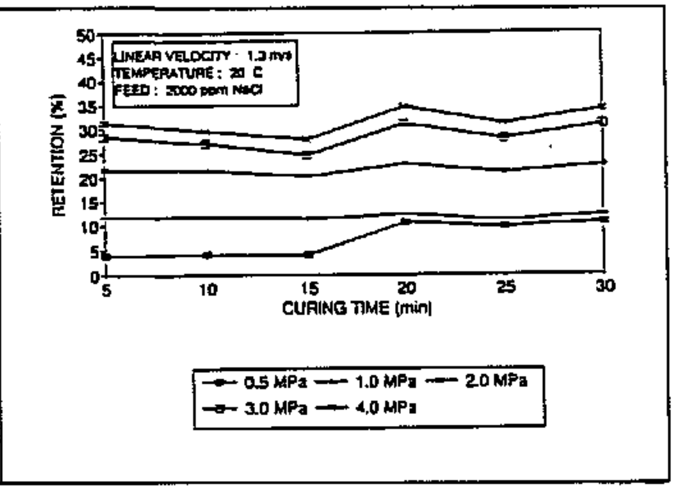
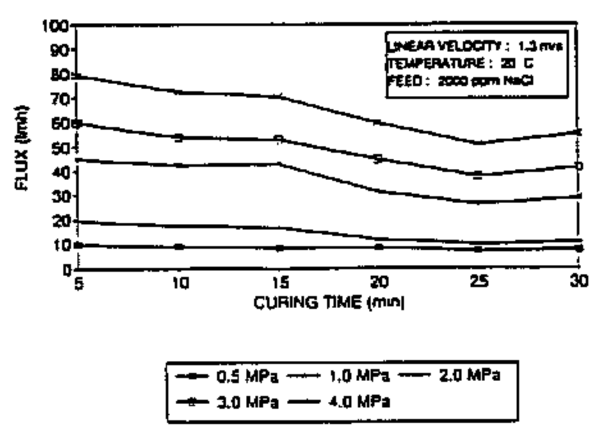


Figure 18:
Effect of curing time on NaCl retention at different pressures. (Solution 1 at 80 °C)



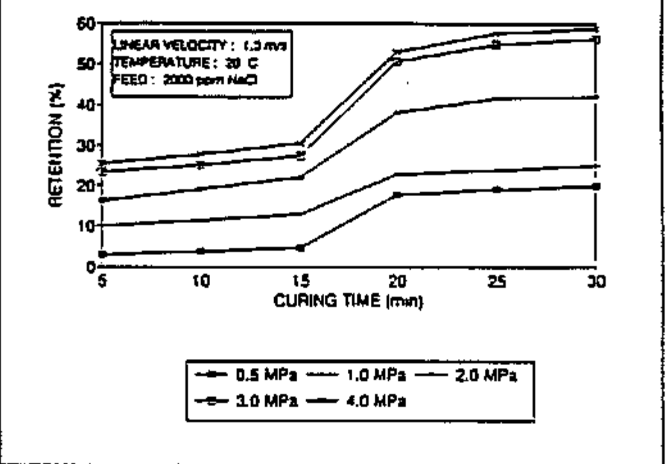


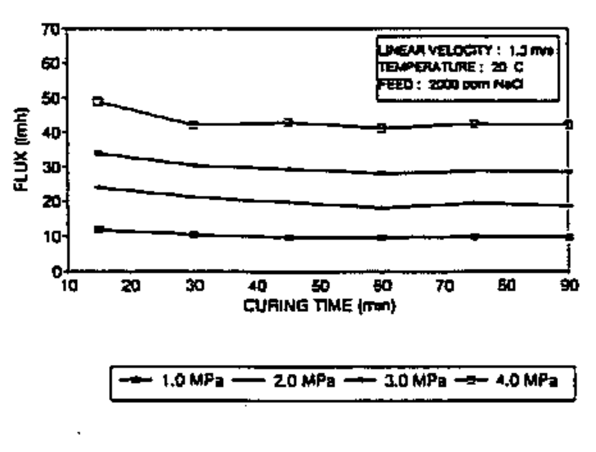
Figure 19:
Effect of curing time on permeate flux at different pressures. (Solution 2 at 80 °C)

Figure 20:
Effect of curing time on NaCl retention at different pressures. (Solution 2 at 80 °C)

(b) Curing at 60°C

An increase in the curing time at 60 °C did not have a very marked effect on the permeate fluxes of membranes made from either of the two solutions, and only a slight decrease in flux was observed for membranes made from Solution 1 (Figure 21). With the second solution, the flux increased slightly with increase in curing time at this temperature (Figure 23).

For both solutions the graphs show an increase in retention as the curing time (at 60 °C) is increased from 15 to 90 minutes (Figures 22 and 24).



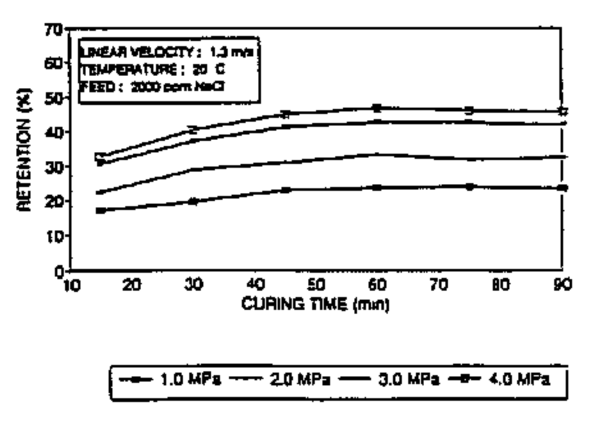


Figure 21:
Effect of curing time on permeate flux at different pressures. (Solution 1 at 60 °C)

Figure 22:
Effect of curing time on NaCl retention at different pressures. (Solution 1 at 60 °C)

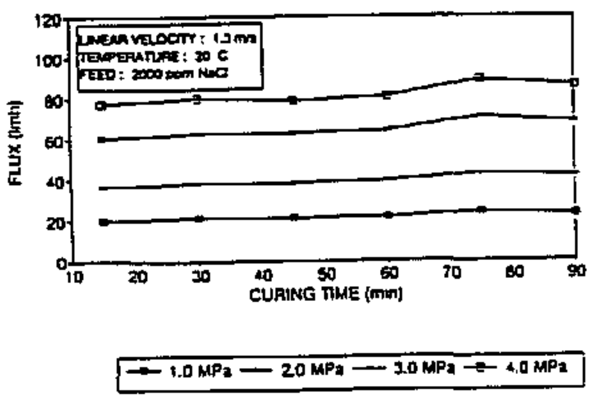


Figure 23:
Effect of curing time on permeate flux at different pressures. (Solution 2 at 60 °C)

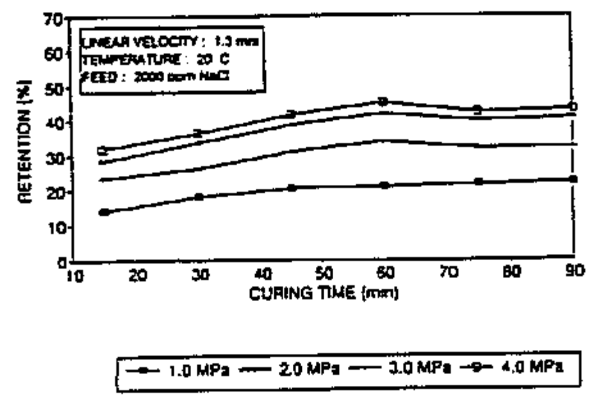


Figure 24:
Effect of curing time on NaCl retention at different pressures. (Solution 2 at 60 °C)

(f) Effect of solution maturation

In section (c) it was seen that the erratic performances of PVAL membranes produced from solutions containing different concentrations of $K_2S_2O_8$ could not be ascribed to any of the parameters discussed previously. During the course of the examination of the effects of various parameters on the properties of PVAL membranes, the PVAL/$K_2S_2O_8$ solutions were prepared as the need for them arose, or as soon as supports or chemicals became available. Some membranes were thus produced from "old" PVAL solutions while others in the same series from fresh or "new" solutions. At the time, it was not realized that this would have any deleterious effect on membrane performance as the solutions were kept at room temperature and showed no physical evidence of change over a few days. Most of the solutions were discarded after a few uses to prevent contamination. It was also assumed that even if the composition of the solution were to change under such mild conditions, effect on the membrane properties would be negligible.

As discussed in section (c), membranes made from solutions prepared only a few days prior to the other solutions gave membranes which had increased salt-retention. This observation, together with the realization that an old undiscarded solution (approx. 2 weeks old) showed signs of discolouration, led to the study of the effect of maturation on the chemical composition of PVAL/$K_2S_2O_8$ solutions. Only the effect of this process on membrane performance will be discussed here. The results obtained after an investigation into the chemical and physical changes occurring in the PVAL/$K_2S_2O_8$ solutions are described in Addendum 2, Chapter 6.

Firstly, the effect of the $K_2S_2O_8$ concentration on membrane properties were reinvestigated, using solutions prepared simultaneously. The solvation of the PVAL took up to 3 days, depending on the temperature, the molecular mass and the degree of hydrolysis of the PVAL. As mentioned before, it was necessary to cool the PVAL solutions to room temperature before the $K_2S_2O_8$ was added. It was also necessary to add $K_2S_2O_8$ to all solutions simultaneously to produce membranes which would give comparable results.

Thus, 3 % PVAL solutions were prepared and $K_2S_2O_8$ added at concentrations ranging from 0,1% - 3,0%. Three sets of membranes were made:

A: Membranes made as soon as the $K_2S_2O_8$ was dissolved (day 0).

B: Membranes made after 3 days of maturation.

C: Membranes made after 7 days of maturation.

Membranes made from older solutions are always darker in colour than those made from unmatured solutions; colours varied from white, to yellow, to light brown.

The membranes were tested on two different feed solutions containing 2 000 ppm NaCl and 1 000 ppm $MgSO_4$. Figures 25 to 28 show that the maturation of the PVAL/$K_2S_2O_8$ solutions had a significant effect on the salt-retention properties of the membranes. The legends in Figures 25 to 28 refer to the time the solutions were matured prior to membrane fabrication.

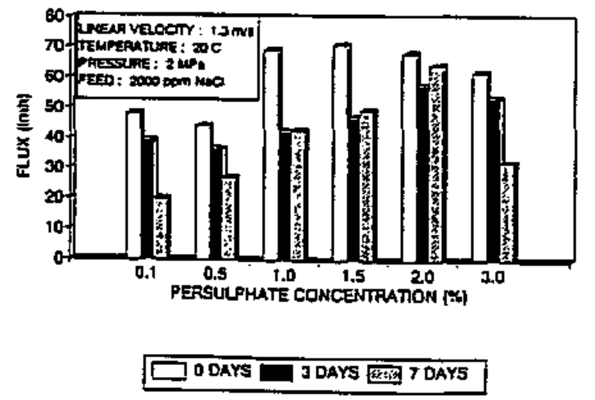


Figure 25:
Effect of solution maturation time on permeate flux at different persulphate concentrations

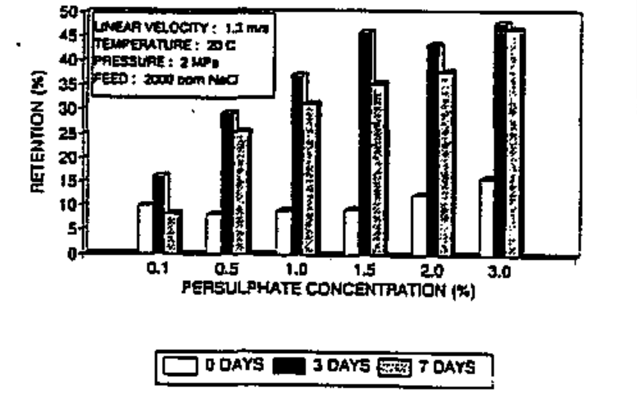


Figure 26:
Effect of solution maturation time on NaCl retention at different persulphate concentrations

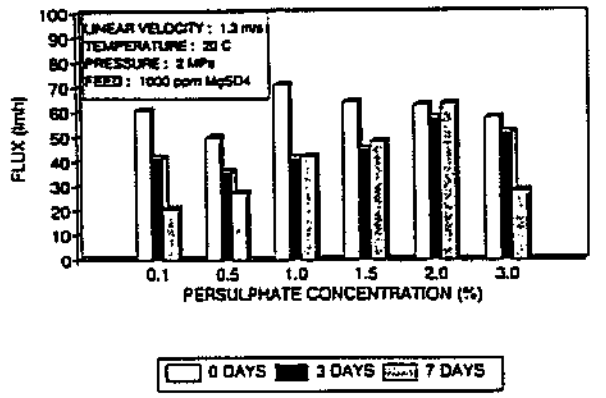


Figure 27:
Effect of solution maturation time on permeate flux at different persulphate concentrations

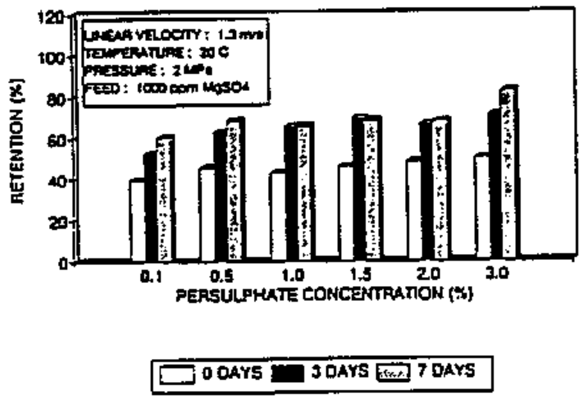
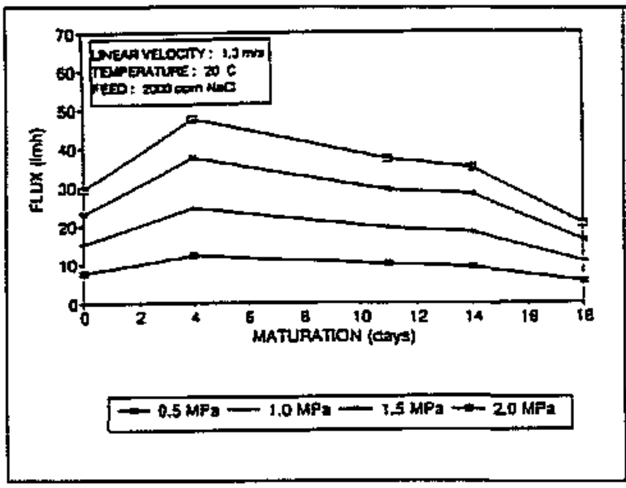


Figure 28:
Effect of solution maturation time on MgSO4 retention at different persulphate concentrations

It was evident that by maturing the PVAL/$K_2S_2O_8$ solutions for only 3 days the NaCl retention of subsequent membranes increased almost 5-fold increase (9,4% to 46%), while the flux decreased from 1 700 lmd (71 lmh) to 1 130 lmd (47,1 lmh). It has thus been established that the erratic results obtained previously were most probably due to the maturation of some of the PVAL/$K_2S_2O_8$ solutions prior to membrane making, as the results in Figures 25 to 28 do not show the discrepancies seen in section (c).

The slightly lower retentions and higher fluxes of the membranes made from the 7-day-old solutions (compared with solutions matured for 3 days) could be attributed to the fact that, out of necessity, the "7 day" membranes were made on 546T supports while the other membranes were made on 719 supports. The MEMBRATEK 719 support membranes have higher salt retentions and lower fluxes than the 546T membranes.

The study of the effect of solution maturation was repeated using only one PVAL/$K_2S_2O_8$ solution containing 3 % PVAL and 1,5 % $K_2S_2O_8$. MEMBRATEK 719 supports were used. Membranes were made from the ageing solution at regular intervals, with a maximum maturation time of 18 days, after which gelling occurred. The membranes were evaluated at pressures ranging from 0,5 to 2 MPa with feeds containing 2000 ppm NaCl and 1000 ppm $MgSO_4$ respectively. The results appear in Figures 29 to 32, which show the effect of maturation on the properties of the membranes.



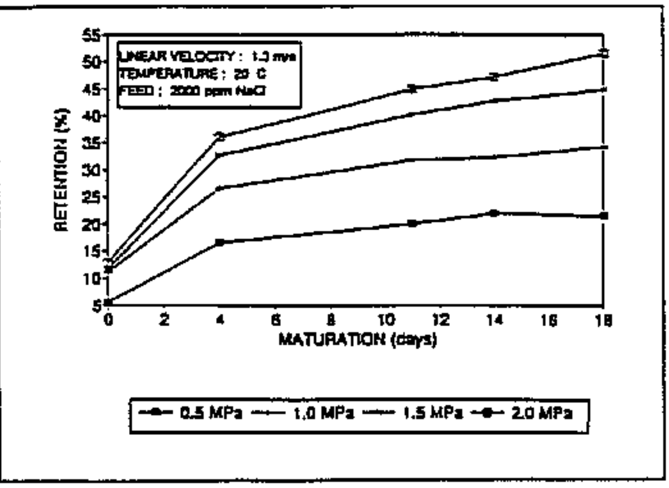
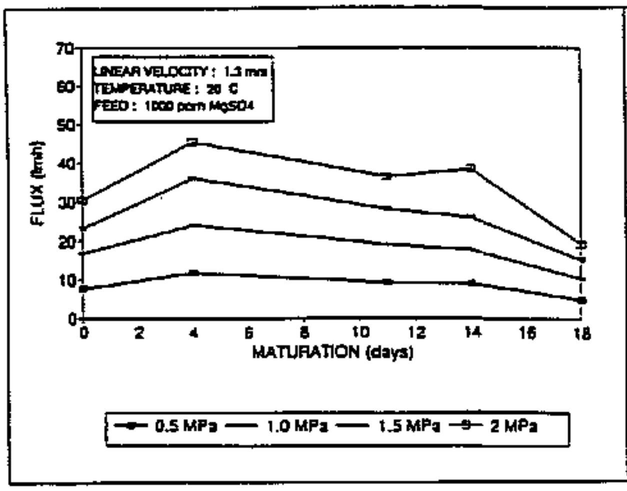


Figure 29:
Effect of solution maturation on permeate flux at different pressures

Figure 30:
Effect of solution maturation on NaCl retention at different pressures.

The NaCl retention increased by more than 300 % when the solution was matured for 18 days (Pressure = 2 MPa). The flux, however, increased as the solution was matured for 0 - 4 days, reached a maximum for maturation of 4 - 11 days and then decreased as the solution was matured further to 18 days. The $MgSO_4$-retention properties followed the same basic trends as the NaCl, but the effect was not as pronounced. The $MgSO_4$ retention increased from 59,5 to 85,9 % when the solution is matured for 18 days (See Figure 32). Figure 31 is similar in trend to Figure 29, in which the flux increased to a maximum value, after which it decreased with further maturation.



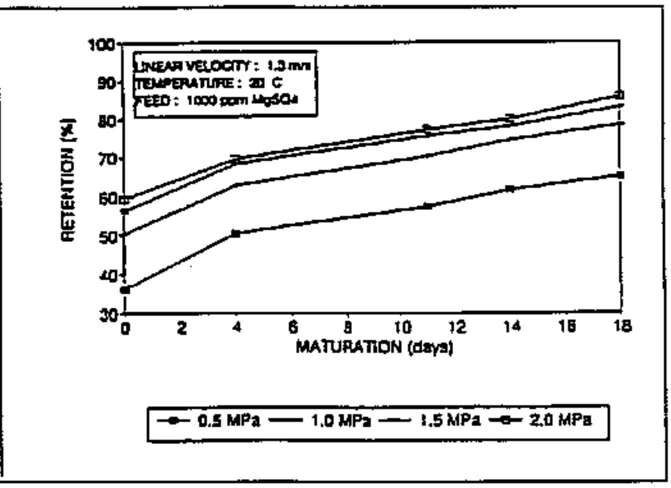


Figure 31:
Effect of solution maturation on permeate flux at different pressures

Figure 32:
Effect of solution maturation on $MgSO_4$ retention at different pressures

The membranes mentioned above were evaluated at the end of 1991 and were kept in the test rig over the summer vacation. A 4g/l formaldehyde solution was pumped through the membranes to prevent algal growth. After standing for a month, the membranes were re-evaluated under the same conditions. The results are given in Figures 33 to 36.

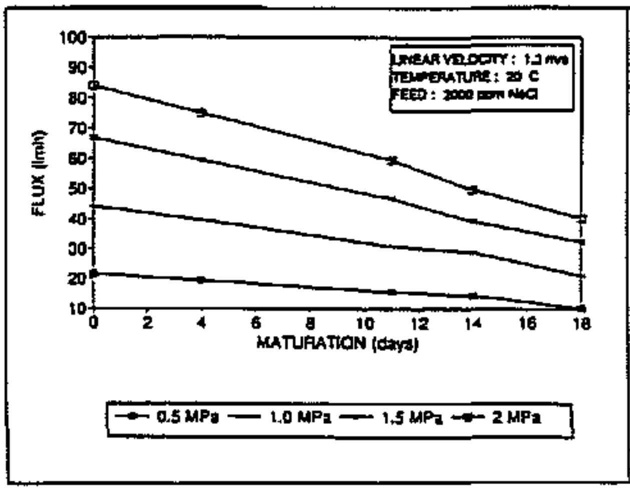


Figure 33:
Effect of solution maturation on permeate flux at different pressures

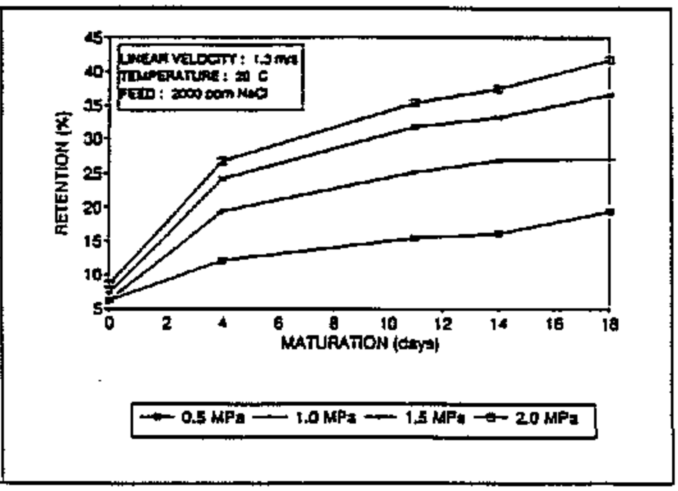


Figure 34:
Effect of solution maturation on NaCl retention at different pressures

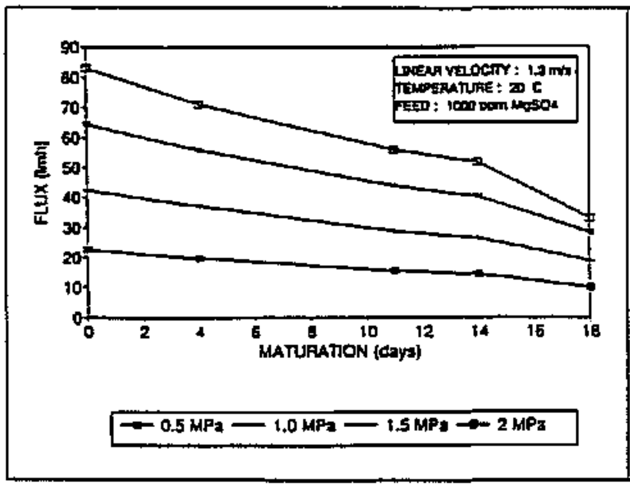


Figure 35:
Effect of solution maturation on permeate flux at different pressures

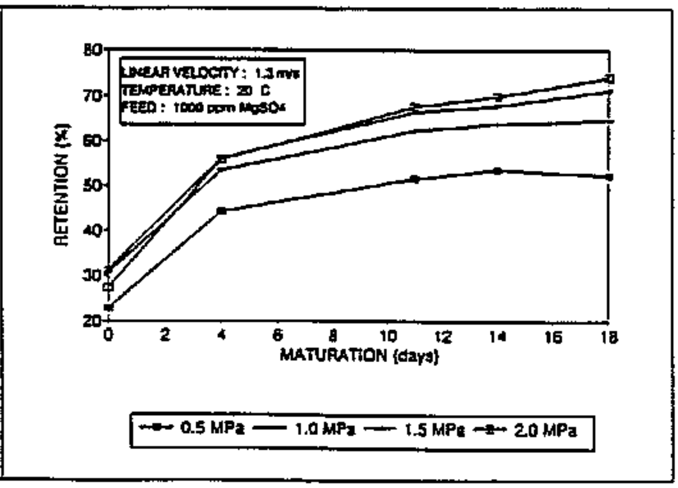


Figure 36:
Effect of solution maturation on MgSO4 retention at different pressures

A dramatic change in membrane properties can be seen in Figures 33 and 34 (compared to 29 and 30). The fluxes of membranes made from the unmatured solutions increased more than those of membranes made from the matured solutions. This indicated that, when maturation times were short, the membranes were not very stable, which resulted in the large increase in flux with operating time. The salt retentions of the membranes showed only a 20% decrease (42% compared with 52% NaCl retention at 2MPa, 2% $K_2S_2O_8$, 18 days matured). When Figures 35 and 36 are compared with Figures 31 and 32, the trends are the same for a feed of 1000 ppm $MgSO_4$.

The membranes made from the solution comprising 3% PVAL and 1,5% $K_2S_2O_8$ which had been matured for 18 days, were (after the second test), subjected to evaluation on an oversaturated feed solution of $CaSO_4$ for about 600 h, to determine their robustness and permanence. The solution contained of 10 000 ppm $CaSO_4$, and since the solubility of $CaSO_4$ is approximately 2,8g/l, the feed contained approximately 7,2g/l undissolved crystals. Figure 37 shows the permeate flux and retention values of this membrane.

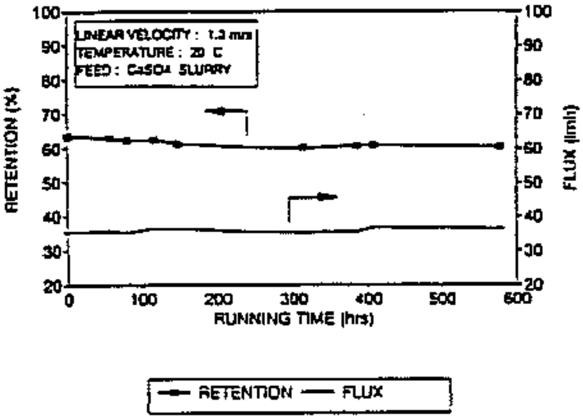


FIGURE 37:
Test results of PVAL/$K_2S_2O_8$ membranes with $CaSO_4$ slurry versus test time

It was evident that the retention decreased slightly and then reached a limiting value at about 60%. The flux values vary slightly between 840 lmd (35 lmh), and 890 lmd (35 lmh). This test shows that the crosslinked PVAL/$K_2S_2O_8$ membranes are resistant to abrasion by slurry feeds for at least 600 hours. It should be noted that the membranes used in this test had been subjected to rigorous treatment beforehand, including several tests on NaCl and $MgSO_4$ feeds and storage for one month in a formaldehyde solution to prevent algal growth. Newer membranes are expected to give higher $CaSO_4$ retentions (> 80%).

(g) Effect of glycerol pre-treatment

(i) Support membranes

It is well known that the porous structure of polysulphone and polyethersulphone membranes is destroyed when they are dried out, especially at elevated temperatures. For this reason these membranes were always stored in water. When membranes are used as support membranes (for the production of composite RO and UF systems), the thin film deposited on the surface often needs curing at temperatures ranging from 60 - 150°C. If, in such cases, the support has not been adequately treated beforehand, the fluxes will be very low due to the collapse of the support structure. To avoid this problem, a wetting agent is often used to prevent the support membrane from drying out completely. Table 20 tabulates the procedures followed in an experiment designed to determine the effect of a wetting agent, in this case glycerol, on the water-transport properties of M719L membranes obtained from Membratek.

TABLE 20:

Glycerol treatment procedures

Code	Pre-drain[1]	Glycerol[2]	Drain[3]	Air Dry[4]	Heat-treatment[5]
W	X				
B	X				X
GB	X	X	X		X
GA	X	X	X	X	
GAB	X	X	X	X	X

1. The membranes were removed from storage in water and drained vertically for 2 min.
2. Glycerol treatment involved the storage of the membranes in a 50% glycerol/water mixture for 24 h to ensure complete wetting.
3. This drainage was to remove the excess glycerol solution from the membrane (2 min).
4. This step involved drying of the glycerol treated membranes at room temperature for 3 days.
5. These membranes were heat treated in a vertical oven @ 80°C for 20 min.

Figures 38 to 41 show the results of RO tests on these membranes on water at pressures ranging from 0,5 - 2,0 MPa.

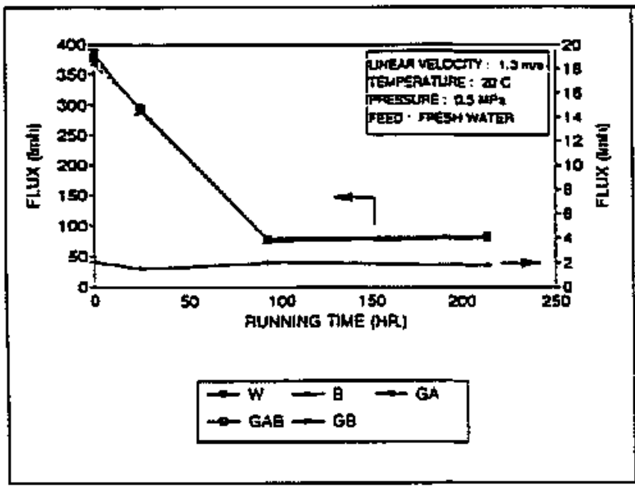


Figure 38:
Effect of glycerol pre-treatment on permeate flux at 0.5 MPa

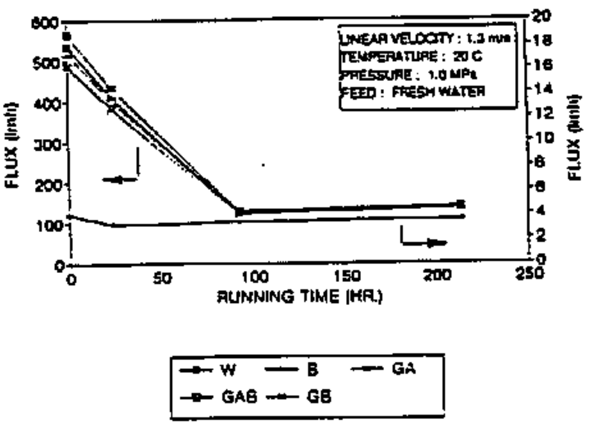


Figure 39:
Effect of glycerol pre-treatment on permeate flux at 1.0 MPa

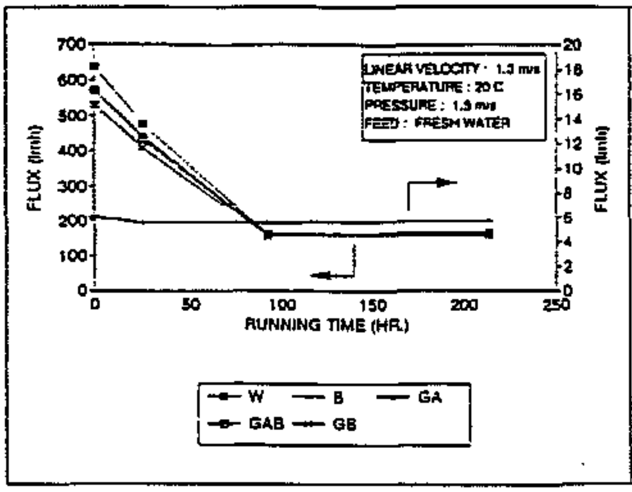


Figure 40:
Effect of glycerol pre-treatment on permeate flux
at 1.5 MPa

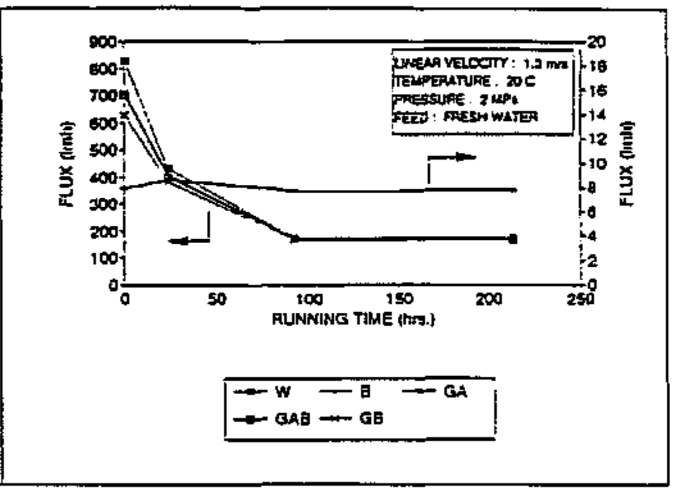


Figure 41:
Effect of glycerol pre-treatment on permeate flux
at 2.0 MPa

The flux of membrane B (membrane without any prior glycerol treatment) stayed fairly contstant at about 192 lmd (8 lmh) (tested at 2 MPa), as seen in Figure 41. The flux of the control membrane (W), on the other hand, started off at a value exceeding 800 lmh (Flux (W) > 100 x Flux (B) !), and decreased steadily to 174 lmh after 92 h at which it levelled off for the remainder of the test.

The remaining three membranes, all of which were treated with glycerol before being heated, initially gave slightly lower fluxes (620 to 700 lmh), but they also decreased to values similar to that of the untreated membrane. This shows that the water-transport properties of the M719L ultrafiltration membranes were destroyed by heat-treatment if a suitable wetting agent was not used. Fluxes equal to those of the original membranes could, however, be achieved if the membranes were treated with glycerol before being heat treated. Comparison of the fluxes of membranes GB and GAB showed that the additional air-drying step resulted in a higher initial flux, and when those of membranes GA and GAB were compared, the similar fluxes obtained indicated that heat treatment of membrane GA at 80 °C for 20 min had a negligible effect on its performance.

Figure 42 shows a hysteresis effect, whereby fluxes obtained when the pressure was increased from one value to the next was higher than those obtained when the pressure was decreased (control membrane W). The same effect was observed with all the glycerol-treated membranes, but not with membrane B (Figure 43).

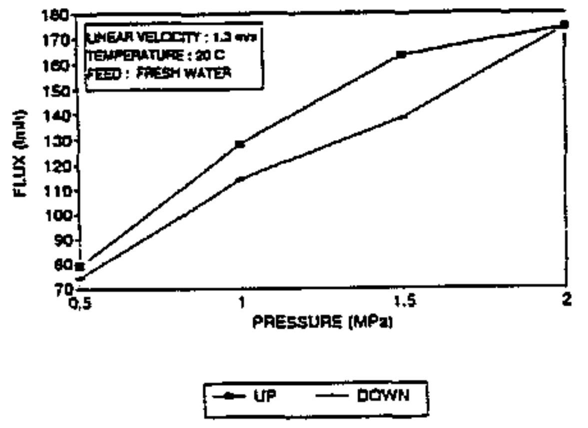


Figure 42:
Effect of increase and decrease in pressure on permeate flux of control membrane

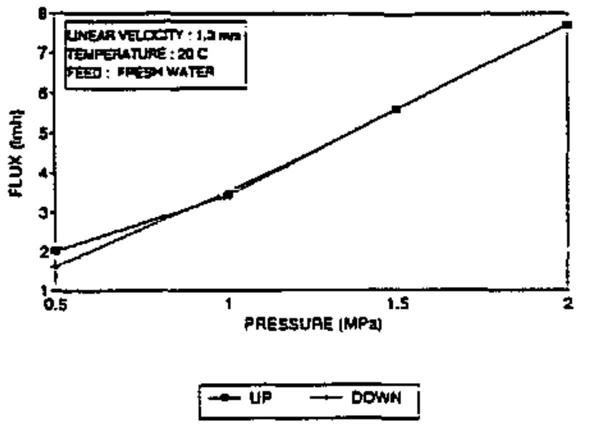


Figure 43:
Effect of increase and decrease in pressure on permeate flux of untreated membrane (B)

(ii) PVAL/$K_2S_2O_8$ membranes made on glycerol treated supports

PVAL/$K_2S_2O_8$ membranes were made on glycerol-treated supports (GA) and compared with those made on untreated M719L support membranes. Solutions containing 3% PVAL and 1,5% $K_2S_2O_8$ were matured for 35 days and used to coat both types of supports. The six different grades of PVAL used are listed in Table 21.

TABLE 21:
Grades of PVAL used to prepare PVAL/$K_2S_2O_8$ membranes on glycerol treated supports

Code	Mol. Mass	% Hydrolysis	Supplier
A	15 000	86-89	Fluka
B	72 000	88	Unilab
C	125 000	87-89	BDH
D	14 000	100	Aldrich
E	72 000	> 98	Merck
F	115 000	100	Aldrich

Membranes made on untreated M719L supports are labelled A1, B1, C1, D1, E1 and F1, while those coated onto glycerol treated support membranes are labelled A2, B2, C2, D2, E2 and F2, depending on which of the six grades of PVAL was used. A third set of membranes, A3, B3, C3, D3, E3 and F3, was made on untreated supports from neutralized solutions to determine the effect of the pH of the solution on membrane properties. The basic fabrication conditions in Table 17 were used to produce all these membranes.

Figures 44 and 45 show fresh water flux values at different pressures for membranes prepared on untreated and glycerol treated membranes respectively.

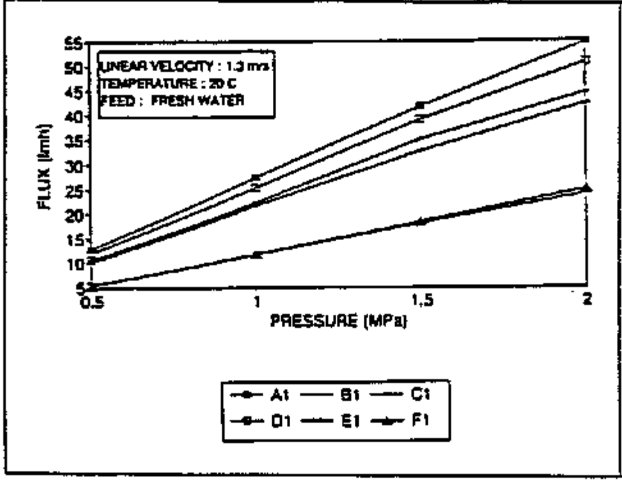


Figure 44:
Effect of pressure on permeate flux of membranes made on untreated supports from different grades of PVAL

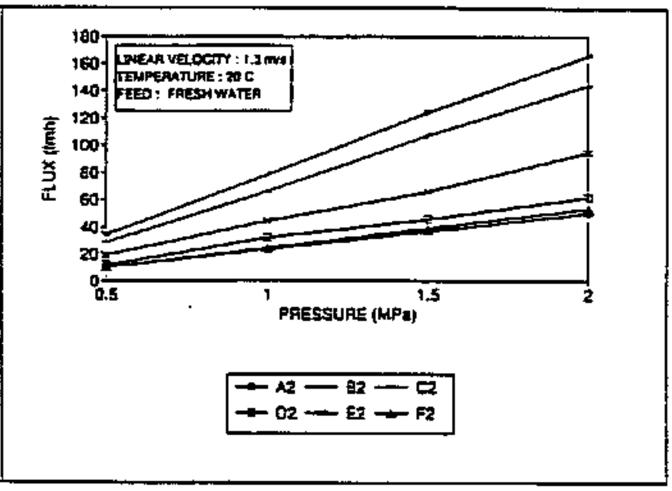


Figure 45:
Effect of pressure on permeate flux of membranes made on glycerol treated supports from different grades of PVAL

It can be seen that the untreated supports yielded PVAL membranes with flux values much lower than those obtained from membranes made from glycerol-treated supports. These fluxes were, however, not nearly as low as the 192 lmd (8 lmh) obtained (in section (g)) from untreated supports heat-treated without glycerol. This indicates that the PVAL itself acted as a wetting agent, but obviously not to the same degree as glycerol.

This phenomenon was expected because of:

(a) the similar chemical structure of PVAL and glycerol (both hydrophilic multifunctional alcohols with strong H-bonding capability);

(b) the larger size of the PVAL macromolecule compared with that of glycerol, and

(c) the lower hydroxyl/carbon ratio of PVAL compared with that of glycerol.

After the fresh-water flux test, the PVAL/$K_2S_2O_8$ membranes were tested on a feed solution containing 2 000 ppm NaCl. As expected, the fluxes of all the membranes (Figures 46 and 47) dropped slightly because of an increase in osmotic pressure.

When the NaCl retentions were compared (Figures 48 and 49) it was clear that the advantage gained in flux by pre-treatment of PVAL membranes with glycerol was lost in salt retention. The doubling of flux values due to glycerol treatment was unfortunately accompanied by an approximately 50% reduction in NaCl retention. Figures 50 and 51, depicting flux and retention values at 2 MPa, clearly shows the effect that the grade of PVAL has on the salt-retention properties of the membranes.

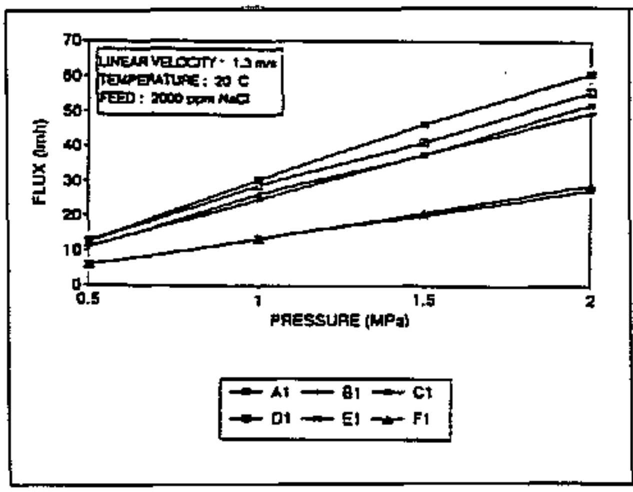


Figure 46:
Effect of pressure on permeate flux of membranes made on untreated supports from different grades of PVAL

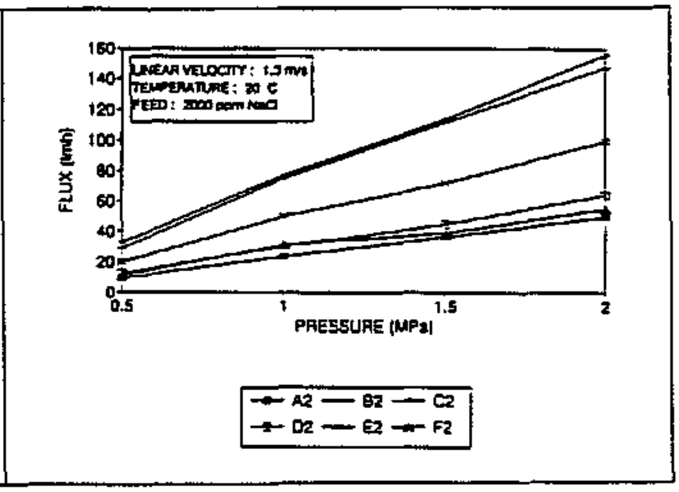


Figure 47:
Effect of pressure on permeate flux of membranes made on glycerol-treated supports from different grades of PVAL

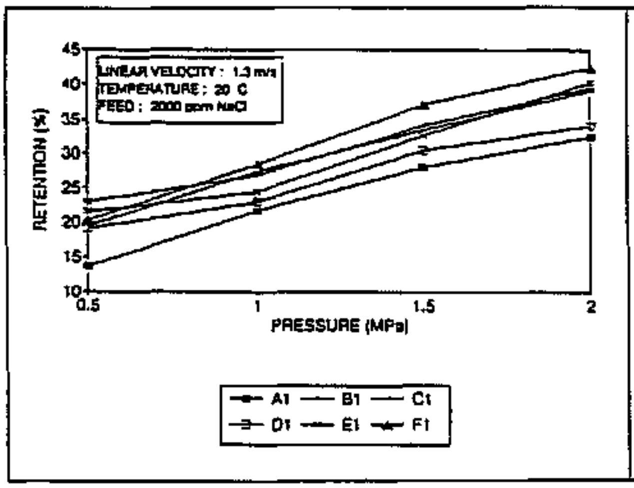


Figure 48:
Effect of pressure on NaCl retention of membranes made on untreated supports from different grades of PVAL

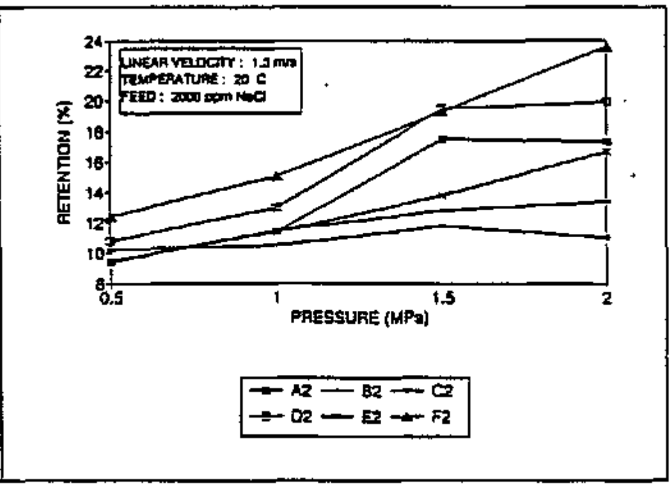


Figure 49:
Effect of pressure on NaCl retention of membranes made on glycerol-treated supports from different grades of PVAL

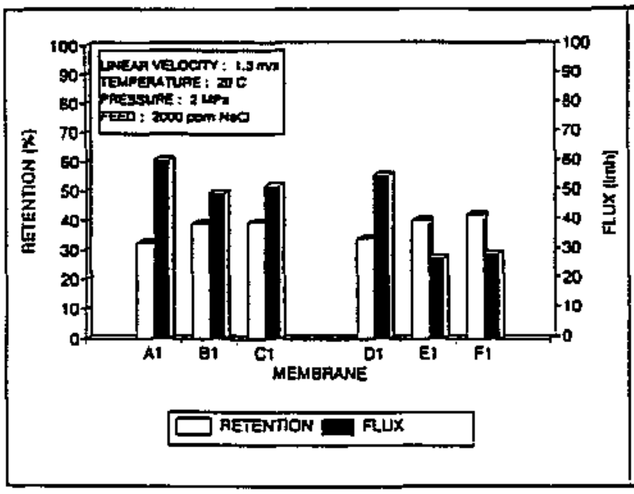


Figure 50:
Effect of the grade of PVAL used in the production of membranes on their NaCl retention and permeate flux. (Untreated supports)

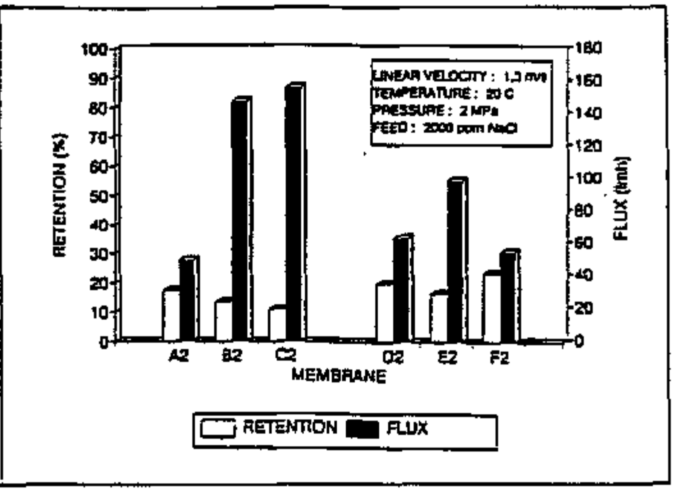


Figure 51:
Effect of the grade of PVAL used in the production of membranes on their NaCl retention and permeate flux. (Glycerol-treated supports)

The matured solutions used in the fabrication of membranes A1..F1 and A2..F2 had a pH of approximately 1,1. To establish the effect of the low pH on membrane properties, the solutions were neutralized (pH=7) before the fabrication of membranes A3..F3. The results are shown in Figure 52.

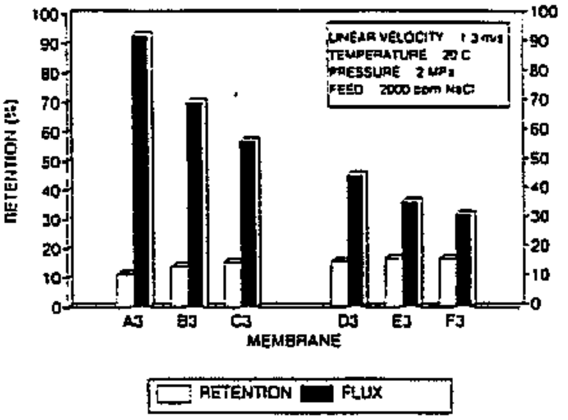


FIGURE 52:

Performance of membranes made on untreated supports from neutralized PVAL/$K_2S_2O_8$ solutions

When compared with the results obtained from membranes made from the non-neutralized solutions, it was evident that membranes A3..F3 exhibited much lower salt retentions and higher fluxes. It was also observed that the membranes made from the neutralized solutions were much lighter in colour that membranes A1..F1. It was therefore concluded that the acidity of the PVAL/$K_2S_2O_8$ solution played an important role in the crosslinking chemistry during the heat-curing of PK type membranes.

Characterization of Maturing PVAL/$K_2S_2O_8$ solutions

It has been shown that matured PVAL/$K_2S_2O_8$ solutions produce membranes with higher salt-retentions than those made from unmatured solutions of similar composition. Several techniques, including viscometry, UV spectrophotometry, NMR spectroscopy, and pH measurement were used to characterize the changes which occurred in maturing PVAL/$K_2S_2O_8$ solutions in order to obtain a better understanding of the reasons for this apparent improvement in membrane properties. These results have been given and discussed in Addendum 2, Chapter 6.

Treatment of Industrial Wastewater

The PVAL/$K_2S_2O_8$ membranes, together with amine modified PVAL membranes were evaluated on raw industrial effluent cooling water blowdown (CWBD) for the SASOL plant in Secunda.

Results are presented in section 2.4.4.

2.3.3.4 Conclusions

1. PES-PVAL gel-layer composite membranes could be formed by depositing aqueous solutions of PVAL and $K_2S_2O_8$ on asymmetric PES substrate membranes. The PVAL coatings were insolubilized by crosslinking during heat treatment at 60 - 100°C. The gels were highly hydrophilic, but water-insoluble. The fact that the gel was not destroyed hy heating in acidic and basic solutions indicated that crosslinking occurred through formation of covalent (carbon-carbon) bonds.

2. The influence of several variables on the RO performances of PES-PVAL gel-layer membranes was investigated. It was found that PVAL concentration, $K_2S_2O_8$ concentration, curing time and curing temperature played a significant role in determining the extent of crosslinking and, consequently, RO properties. A simple manipulation of one or more of these variables resulted in membranes with widely differing salt-retention and water permeability characteristics.

2. Potassium persulphate ($K_2S_2O_8$) can be used to crosslink PVAL to form insoluble nanofiltration membranes on tubular polyether sulphone (PES) substrates. PVAL/$K_2S_2O_8$ solution maturation time was found to be a most important variable which effected the salt retention properties of a membrane.

3. The concept of maturing PVAL/$K_2S_2O_8$ solutions prior to use in membrane fabrication led to improved salt retentions, and improved membrane stability. Various spectroscopic and other analytical techniques showed that the following changes occurred in the maturing solutions:
   (a) the degree of hydrolysis of the PVAL increased with increased maturation,
   (b) polyene keto groups were formed in the backbone of the polymer,
   (c) gelation of the polymer was most likely caused by the coupling of polymer radicals to form carbon-carbon bonds.

   Membranes made by the insolubilization of PVAL with $K_2S_2O_8$ gave the following salt-retention properties:

50% retention; 960 lmh flux	2000 ppm NaCl; 2 MPa; 20°C; 1,3 m/s
75% retention; 960 lmh flux	1000 ppm $MgSO_4$; 2 MPa; 20°C; 1,3 m/s

4. These membranes also were evaluated on real effluents to study their performance and fouling characteristics. PVAL-$K_2S_2O_8$ gel-layer membranes were resistant to abrasion when tested on a $CaSO_4$ slurry feed for about 600 h. Laboratory and field trials on an industrial effluent have underscored the robustness and chemical resistance of these membranes.

5. Further results of studies have indicated that the PES-PVAL gel-layer composite membrane system could also function as medium-retention, high-flux RO membranes at relatively low operating pressures of 1 to 2 MPa, even in the absence of an interfacially formed salt-retention barrier.

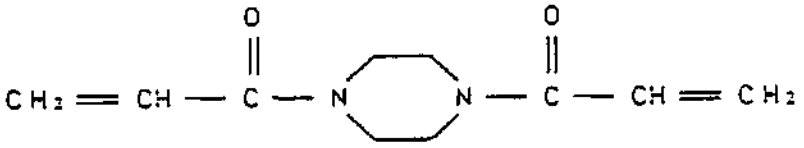
6. For desalination by RO, an ultrathin salt-retention barrier will ultimately be formed on the PVAL gel layer by interfacial polycondensation, see section 2.4. Therefore, high salt-retention capability is not a prerequisite, and coating solution compositions and fabrication conditions can be adjusted to give high-flux gel layers. For this purpose, curing temperatures of 80 - 90°C and short curing times are recommended.

2.3.4 INSOLUBILIZATION OF POLY(VINYL ALCOHOL) BY CROSSLINKING WITH MULTIFUNCTIONAL ACTIVATED VINYL COMPOUNDS

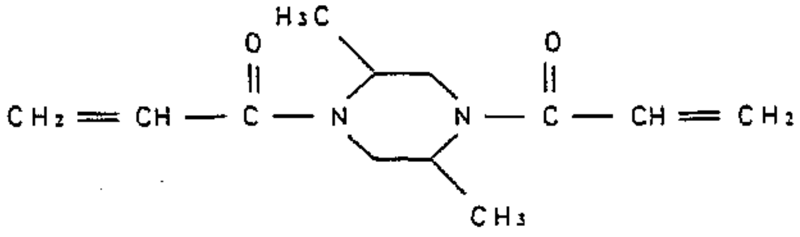
2.3.4.1 Background

The insolubilization of PVAL in the presence of peroxydisulphate (discussed in Section 2.3.3) has proved to be a convenient method for the preparation of stable hydrophilic gel-layer membranes. Although membranes prepared by this crosslinking method might be suitable for nanofiltration applications, their moderate salt-retention capabilities make them unsuitable for low-pressure desalination of, for example, brackish water. In a recent paper on the reverse osmosis properties of these PVAL gel-layer membranes [78], it has been suggested that the selective permeability to water and salts could probably be improved by further chemical modification of the PVAL gel layer.

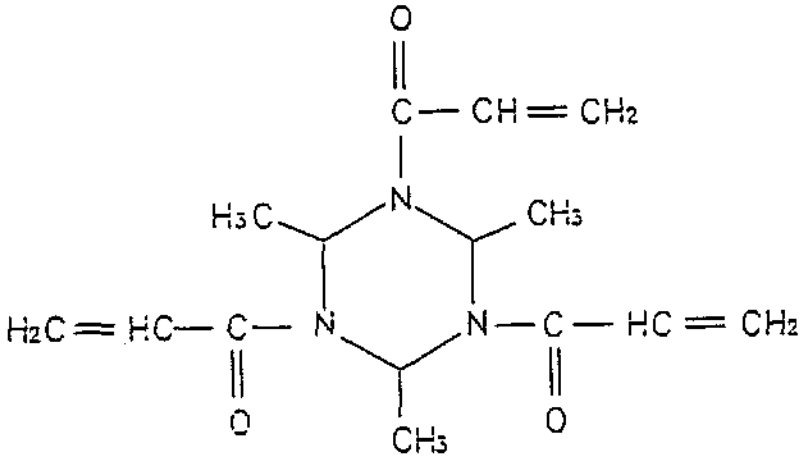
It is known that, apart from the oxidation of hydroxyl groups to form ketones, peroxydisulphate also generates free radicals on the PVAL chain. The gelation of aqueous PVAL solutions during heat treatment is caused by the coupling of these polymer radicals. Structural modification of the PVAL gel should be possible if other reactive compounds, which are capable of participating in free-radical reactions, are added to the membrane coating formulation prior to heat treatment. Compounds containing reactive double bonds, such as vinyl and acrylic monomers, are obviously suitable candidates for the preparation of modified PVAL gels by a free-radical crosslinking mechanism. However, for such vinyl or acrylic monomers to be used as crosslinking agents for PVAL, they must be, at least, difunctional. Since the crosslinking of PVAL must be carried out in an aqueous medium, the crosslinking agent must also be water-soluble. Furthermore, it is believed that the incorporation of amide linkages into the structure of the crosslinked PVAL could lead to improved salt-retention properties. With these requirements in mind, it was decided to synthesize a number of di- and trifunctional activated vinyl compounds and to study their application as crosslinking agents for PVAL in the presence of free-radical initiators. The structures of these multifunctional activated vinyl compounds are given below. Compounds I and II are commonly referred to as bisacrylamides, whereas compound III is a trisacrylamide.



N,N'-Bis(acryloyl)piperazine (I)



N,N'-Bis(acryloyl)-2,5-dimethylpiperazine (II)



N,N',N''-Tris(acryloyl)hexahydro-2,4,6-trimethyl-s-triazine (II)

The objectives of this study were to:

(i) Determine reaction conditions which would favour high yields of the respective crosslinking agents;

(ii) Select procedures which would allow the isolation of products of high purity;

(iii) Characterize the crosslinking agents by techniques such as ^1H and ^{13}C NMR, FTIR, and UV spectroscopy;

(iv) Use compounds I, II and III for crosslinking of aqueous PVAL solutions, in the presence of peroxydisulphate;

(vi) Deposit crosslinked PVAL films on poly(ether sulphone) UF membranes and determine water- and salt-permeability characteristics of the resulting composite membranes; and

(vii) Determine the hydrolytic, oxidation and thermal stabilities of the crosslinked PVAL membranes.

2.3.4.2 Materials and Methods

Materials

AR grade chemicals were used without further purification. Acryloyl chloride (98%), anhydrous piperazine (99%), trans-2,5-dimethyl-piperazine (98%), and hexahydro-2,4,6-trimethyl-s-triazine trihydrate (98%) were purchased from JANSSEN CHIMICA. Triethylamine (98%) was purchased from SAARCHEM. Dichloromethane was dried over $CaCl_2$ and purified by distillation onto 4Å molecular sieve. PVAL samples were supplied by KURARAY CO., Japan. The grades of PVAL used in gel-formation studies were PVAL 117 (degree of polymerization 1750; degree of hydrolysis 98,5%) and POVAL 217 (degree of polymerization 1750; degree of hydrolysis 88%). Potassium peroxydisulphate (98%) was purchased from FLUKA.

Synthesis of N,N'-Bis(acryloyl)piperazine (I)

In a 250 ml two-necked roundbottom flask, equipped with a magnetic stirrer bar, dropping funnel and alcohol thermometer, 11,25 g (0,125 mol) acryloyl chloride was dissolved in 60 ml dichloromethane, and the solution was cooled to 0 - 5°C in an ice bath. A mixture of piperazine (4,3 g; 0,05 mol) and triethylamine (15 ml) was dissolved in 100 ml dichloromethane, cooled in an ice bath, and then added dropwise to the stirred solution of acryloyl chloride in dichloromethane. The addition time was approximately 60 minutes. Precipitation of a white powder occurred upon addition of the piperazine solution. The suspension was stirred magnetically at 0 - 5°C for an additional 2 hours, and was then filtered through a Buchner funnel. The white powder on the filter was identified as triethylamine hydrochloride. The bisacrylamide was soluble in dichloromethane and was isolated by evaporating the solvent in vacuum.

Synthesis for N,N'-Bis(acryloyl)-2,5-dimethylpiperazine (II)

This procedure was similar to that described above. A mixture of 2,5-dimethylpiperazine (2,85 g; 0,025 mol) and triethylamine (8 ml) was dissolved in 50 ml cold, dry dichloromethane. The amine solution was added dropwise to a stirred, ice-cooled solution of acryloyl chloride (5,63 g; 0,063 mol) in dichloromethane over a period of about 30 minutes. The resulting suspension was stirred for an additional 4 hours at 2°C, stored at -10 °C for 24 hours, and filtered through a sintered glass funnel. The product was isolated by evaporating the dichloromethane in vacuum.

Synthesis of N, N', N"-Tris(acryloyl)hexahydro-2,4,6-trimethyl-s-triazine (III)

Attempts to use the abovementioned procedure for the preparation of compound III in dichloromethane have, to date, been unsuccessful, since hexahydro-2,4,6-trimethyl-s-triazine trihydrate is insoluble in cold dichloromethane. Investigations are continuing to find a suitable procedure for the synthesis of this compound.

Characterization of compounds I and II

All starting materials and products will be characterized by NMR, FTIR and UV spectroscopy.

Crosslinking studies

Aqueous solutions, containing different concentrations of PVAL, potassium peroxydisulphate and disacrylamide, were heated in a water bath at 60 - 80°C to study gel formation.

2.3.4.3 Results and Discussion

Synthesis of bisacrylamides I and II

Even in this early stage of the experimental work, it is clear that the synthesis of bisacrylamides I and II could be carried out successfully at low temperature in dichloromethane as solvent. The reaction of acryloyl chloride with the diamines was highly exothermic and apparently the chlorine atoms of the acid chloride reactant were readily displaced at 0 - 5°C. Triethylamine hydrochloride precipitated immediately from the dichloromethane solvent in this reaction. Yields of bisacrylamide products, based on the amount of diamine used, were quite high. (Yields of 70 - 80% were obtained.)

Both the bisacrylamide products were obtained as crystalline solids, which appeared to be of high purity. Bisacrylamides I and II are highly water-soluble, and could easily be mixed with aqueous PVAL solutions.

Synthesis of the trisacrylamide III

The trisacrylamide III could not be prepared by the procedure described for the synthesis of the bisacrylamides. The search is continuing to find a suitable solvent for the synthesis of trisacrylamide III. Another alternative may be the use of the Schotten-Baumann procedure, i.e., direct addition of the acid chloride to the triamine in the presence of a base, which is usually either aqueous sodium hydroxide or pyridine (organic base).

Characterization of bisacrylamides I and II

Analytical investigations are also in progress to obtain ^{13}C nmr spectroscopic characterizations, FTIR and UV spectra of both the starting materials and the products. FTIR and UV spectroscopy can only provide qualitative information about the presence of certain functional groups (e.g., the $CH_2 = CH$ - and - CO - N groups in the case of IR spectroscopy and the $CH_2 = CH - CO$ - chromophore in the case of UV spectroscopy of the respective bisacrylamides).

Crosslinking studies

Both partially hydrolyzed PVAL (88 mol %) and fully hydrolyzed PVAL (98.5 mol %) were evaluated in crosslinking studies. Aqueous solutions, which contained 2 - 5 wt % PVAL, 1 - 2 wt % peroxydisulphate, and 1 - 2 % bisacrylamide, were heated in a water bath to about 80°C. Gelation occurred in all experiments, but some formulations gelled more rapidly than others. When a solution containing 5% fully hydrolyzed PVAL, 2% peroxydisulphate, and 2% bisacrylamide I was heated in a water batch, the aqueous solution was initially clear. At a certain point during heat treatment, gelation of the entire aqueous solution occurred instantly. Portions of this light-yellow gel were removed, dried at room temperature, and swollen again in distilled water. The gel appeared to be stable in an aqueous environment.

To date, the determination of the structures of these crosslinked PVAL gels has not been possible. By definition, crosslinked polymers are insoluble in organic solvents. This makes their characterization by normal NMR techniques impossible. Some structural information could, in the near future, be obtained by solid-state NMR, using the combined techniques of cross-polarization and magic-angle spinning (CP/MAS). Very fine, homogeneous samples are required for the recording of solid-state NMR spectra. It is not known at this stage whether such criteria could be met in the case of dried, crosslinked PVAL gels, which normally have a tendency to be rubbery.

In the case of bisacrylamides I and II as crosslinking agents, it is believed that crosslinked structures such as IV and V can be formed.

2.3.4.4 Recommendations

This study has only recently been initiated, and results on membrane preparations and reverse osmosis properties of composite membranes are not yet available. In furthering this study, emphasis will be placed on the determination of optimum conditions for the free-radical crosslinking of PVAL with multifunctional activated vinyl compounds. The reverse osmosis performance of PVAL membranes prepared from these materials will also be studied in detail.

2.3.5 CHEMICALLY MODIFIED POLY(VINYL ALCOHOL) MEMBRANES

The following approach for chemically modifying PVAL is in the very early stages and therefore the proposed work only is documented here.

2.3.5.1 Research objective

The long-term research objective is to develop thin-film composite PVA-based RO membranes for desalination of brackish water and industrial wastewater. For this purpose, the final composite membrane must have high water permeability and adequate salt-retention capability at low operating pressures of ≤ 2 MPa. It must also exhibit good oxidation resistance (particularly chlorine resistance), hydrolytic stability, and thermal stability.

2.3.5.2 Background and motivation

Crosslinking of PVA by means of heat-activated chemical reactions in aqueous solutions usually results in the formation of hydrophilic gel-layer membranes with relatively high water fluxes and low to moderate salt retentions (section 2.3). Salt-retention properties can be improved by increasing the concentration of crosslinking agent, the curing temperature, and the curing time. However, when more drastic curing conditions are employed, any improvement of salt-retention properties is usually accompanied by an unacceptable decrease in permeate flux. Regardless of the curing conditions employed, it seems unlikely that NaCl retentions of higher than 80% could be achieved in the case of homogenerously crosslinked PVA membranes. On the other hand, crosslinking of PVA by the interfacial method, e.g., with isophthaloyl chloride, also results in membranes with poor RO performance, in terms of low water permeability.

For many years, the various polyamides have been the most attractive candidates for the development of thin-film composite membranes with high salt-retention properties. It is therefore expected that the salt-retention properties of PVA membranes could be improved if amine-containing monomers or oligomers, which are reactive in interfacial crosslinking reactions, are incorporated into the PVA membranes. Present research efforts are aimed at the development of such amine-modified PVA membranes. The following possibilities are being investigated:

(i) The direct chemical modification of PVA to introduce reactive amine functionalities onto the polymer chain, and the interfacial crosslinking of amine-modified PVA with acid chlorides.

(ii) The use of insolubilized PVA gel-layer membranes (particularly those exhibiting high water permeabilities) as hydrophilic substrates (or base layers) for the deposition of novel polyamide salt-retention barriers by interfacial crosslinking/polycondensation reactions.

Obviously, chlorine resistance remains an important objective for new membrane research. Polyamide membranes derived from primary diamines to the presence of chlorine in feedwater. The higher degree of chlorine resistance of various poly(piperazine amide) membranes is presumably due to the fact that they contain no amidic hydrogens, since they are derived from secondary diamines. Multifunctional secondary amine compounds are not readily available commercially, and many of those having polycyclic or heterocyclic structures cannot be used for membrane formation by interfacial methods because they lack solubility in water. The synthesis of reactive multifunctional secondary amines from commercially available starting materials would therefore be of great value for the preparation and study of new chlorine-resistant polyamide membranes. By the same token, modification of PVA to introduce secondary amine groups onto the polymer chain could provide interesting new polymeric materials for the preparation of chlorine-resistant RO membranes.

2.3.5.3 Proposed experimental work

(a) Direct modification of PVA to introduce pendent secondary amine groups

(i) Synthesis of tosylated PVA. (The OH group is a poor leaving group in nucleophilic substitutions, and must therefore be converted to a group which does leave. Tosylate is the leaving group of choice in this reaction.)
(ii) Purification and characterization of tosylated PVA.
(iii) Reaction of tosylated PVA with the nucleophilic alkoxide ion of aminoalcohols to produce compounds containing ether linkages. The aminoalcohols considered in this

study are, e.g., 3-(hydroxymethyl)piperidine and 2-(methylamino)ethanol. Both contain secondary amine groups and primary hydroxyl groups.

(iv) Isolation, purification and characterization of the resulting vinyl alcohol/amino-alkyl vinyl ether copolymers.

(v) The use of amine-modified PVA for the preparation of thin-film composite membranes by interfacial crosslinking with di- and/or triacid chlorides.

(vi) Study the effect of fabrication variables on the RO performance of amine-modified PVA membranes.

(vii) Study the hydrolytic stability and chlorine resistance of the membranes.

(b) Interfacial deposition of novel polyamide salt-retention barriers on insolubilized PVA gel-layer membranes

(i) Synthesis of novel multifunctional secondary amines from commercially available polyhydroxy compounds and aminoalcohols, via a nucleophilic substitution reaction. (Again, the procedure requires the conversion of hydroxyl groups to tosylates, and the reaction of tosylated compounds with the alkoxide ion of an aminoalcohol). The aminoalcohols mentioned in section (a), and hydroxy compounds such as pentaerythritol, diethylene glycol and sorbitol are considered for the synthesis of multifunctional secondary amines.

(ii) Isolation and purification of intermediate compounds and end-products, and their characterization by techniques such ^1H and ^{13}C NMR, FTIR, and melting-point determinations.

(iii) The deposition of aqueous solutions of secondary amine compounds on insolubilized PVA gel-layer membranes, and interfacial crosslinking with di- and/or triacid chlorides.

(iv) The use of secondary diamines for the synthesis of amine-terminated prepolymers, and characterization of the prepolymers.

(v) Deposition of amine-terminated prepolymers on insolubilized PVA gel-layer membranes and interfacial crosslinking with di- and/or triacid chlorides.

(vi) Study the RO performance of membranes prepared by interfacial crosslinking of multifunctional amines and prepolymers on PVA gel layers.

(viii) Study the hydrolytic stability and chlorine resistance of the thin-film composite membranes.

2.3.6 REFERENCES

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2.4 PVAL AND AMINE-MODIFIED PVAL RO AND NANOFILTRATION MEMBRANES

2.4.1 BACKGROUND

This study entailed the preparation, characterization and use of PVAL and amine-modified PVAL for the fabrication of PVAL gel-sublayers and PVAL/polyamide composite UTF membranes. Various methods of insolubilization of PVAL to form the gel-layer, and the RO performances of such membranes have been described in section 2.3. In order to improve upon the salt-retention properties of the PVAL/$K_2S_2O_8$ gel-layer which had shown the best RO performance to date (see section 2.3.3.3), methods for the formation of composite UTF-membranes comprising a polyamide skin over this PVAL gel-sublayer were studied.

PVAL/$K_2S_2O_8$ membranes were modified in two ways:

(i) by depositing a polypiperazine isophthalamide skin on the insolibilized gel layer,

(ii) by reacting a mixture of a PVAL and an amine with a multifunctional acid chloride, and forming a composite membrane.

Polyamide RO membranes are very well known. Polyamide membranes obtained from the condensation of piperazine and isophthaloyl chloride were considered to be durable membranes due to the following properties **[1]**:

(a) the ring structure of piperazine combined with that of the aromatic diacid produces a stiff chain structure, resistant to compaction;

(b) the high water absorption of piperazine suggests good water-transport properties; and

(c) the absence of labile amidic hydrogen atoms in polyamides derived from piperazine suggests greater resistance to chlorine attack.

Results of RO tests with membranes made from poly(piperazine isophthalamide) showed fluxes comparable to cellulose acetate with 98 - 99% salt retention. The high retentions obtained, combined with this polymer's inherent structural and chemical integrity, prompted research into the incorporation of polyamides in membranes made from polyvinyl alcohol to improve the salt-retention properties without reducing the tolerance.

Although the chemical structure of poly(piperazine isophthalamide) is relatively stable, it is nonetheless a linear polymer, so that the hydrolysis of only a few of the amidic bonds can lead to the disintegration of the polymer. A membrane made from a three-dimensional polyamide, on the other hand, will remain intact even if several of the amidic bonds were hydrolyzed.

To produce a three-dimensional polyamide, either or both the amine and acid chloride used in its production should have a functionality of three or more. As will be seen later, in section 4, a trifunctional acid chloride (TMC) produced membranes with poor salt-retention properties. The use of a multifunctional amine was the next obvious step. The structure of polydiallylamine suggests that it possesses similar favourable characteristics as piperazine.

2.4.2 MATERIALS AND METHODS

2.4.2.1 **Materials**

Details of the chemicals used in membrane fabrication have been given in Addendum 2, Chapter 4. The polymerization of diallylamine and characterization of poly(diallylamine) is described in Addendum 2, Chapter 3.

2.4.2.2 **Membrane fabrication**

The PVAL membranes described in this section may be divided into three groups according to the methods used in their fabrication. The first membrane type (Type Code: PK) is formed by the insolubilization of polyvinyl alcohol using potassium persulphate. In the fabrication of the second type (Type Code PKPA), a polyamide membrane is deposited over the crosslinked PVAL of the PK-type membrane to form a composite polyamide membrane with a PVAL gel sublayer. A variation of this approach, whereby the PVAL and amine are deposited in one step, leads to the formation of the third membrane type (Type Code PPA). Classification of PVAL membrane types is tabulated in Table 22 in an attempt to give a clear indication to the procedure and materials used in their fabrication. The type codes refer to the general classes of membranes, e.g., PKPA membranes are made from PVAL, $K_2S_2O_8$, and a polyamide (PA). The membrane codes give an indication of the type of amine used in the polyamide, so that PPIP membranes are made from PVAL and Piperazine, and PPDAA membranes from PVAL and PDAA. The exclusion of the letter K from the codes indicates that $K_2S_2O_8$ was not used to crosslink the PVAL prior to the deposition of the polyimide.

TABLE 22:
Classification of PVAL-membrane types

TYPE CODE	MEMBRANE CODE	FABRICATION METHOD			
		PVAL	$K_2S_2O_8$	AMINE	ACID CHLORIDE
PK	PK	Yes	Yes	NO	NO
PKPA	PKPIP	Yes	Yes	PIP	IPC
PPA	PPIP	Yes	No	PIP	IPC/TMC
	PPDAA	Yes	No	PDAA	IPC

Since many membranes of each type were produced to find the best conditions for formation, only the basic techniques involved in the fabrication of the three different types of membranes will be described here. Details of specific fabrication conditions will be found in the results and discussion section (2.4.3), and in section 2.3.3.3 for the PK/$K_2S_2O_8$ membranes.

PK Membranes

The preparation of PVAL/$K_2S_2O_8$ solutions and fabrication of membranes has been described in section 2.3.3.2.

PKPA Membranes

Solution preparation: Two solutions were required for the formation of the PKPA polyamide membrane. The first was an aqueous solution containing the amine (piperazine) and a suitable acid scavenger (TEA) to neutralize the acid liberated during polycondensation reaction. The second was a solution of the diacid chloride (IPC) in hexane. Both solutions were made up in Schott bottles using magnetic stirrer plates.

Membrane fabrication: The fabrication of these membranes involved the deposition of a polypiperazine isophalamide membrane on top of the crosslinked PVAL/$K_2S_2O_8$ membrane. The PVAL/$K_2S_2O_8$ membranes were dipped first into an aqueous solution containing the PIP, drained of excess solution, and subsequently dipped into a solution of the IPC in hexane to form the polyamide membrane at the interface of the two immiscible solvents. After the drainage of the second solution, the membranes were cured at elevated temperatures to complete the polycondensation reaction.

PPA Membranes

Solution preparation: In the fabrication of these membranes the aqueous solution contained both the PVAL and the amine, so that both substances could be applied to the surface of the UF support in one step. The PVAL solution was made according to the procedure decribed in 2.3.3.2, but without the addition of the $K_2S_2O_8$. The amine (PIP, TAB or CPA) and acid-acceptor (NaOH) were then dissolved in the PVAL solution prior to filtration. The organic solution consisted of the multifunctional acid-chloride (IPC or TMC) in hexane. When PDAA was used as the amine, the procedure had to be adjusted to allow for the insolubility of PDAA at low pH levels created by the addition of the acid scavenger. Four solutions were prepared. The aqueous solution containing the PVAL and PDAAP was made according to the general procedure but with the omission of the acid-acceptor. Two separate solutions containing the acid-scavenger were then prepared, one containing NaOH in water, and the other containing TEA in hexane. The fourth solution consisted of the crosslinking agent (IPC) in hexane.

Membrane fabrication: All the PPA type membranes, with the exception of those made with PDAA, were prepared by dipping M719-L supports into the PVAL/amine/scavenger solution, draining, and then dipping them into the crosslinking solution. They were then air dried before curing at elevated temperatures in the vertical oven. The preparation of the membrane based on PDAA, involving the use of three or four solutions described above, will be discussed in the following section 2.4.3.3(b).

2.4.2.3 Membrane evaluation

RO test rig

The equipment used for the evaluation of membranes is shown schematically in Figure 53. The feed solution was circulated through the membrane test rack by a HYDRACELL D10 diaphragm pump before being returned to the feed tank. The volumetric flow rate was measured on the rotameter, whilst the inlet and outlet pressures where monitored on the pressure gauges P1 and P2 respectively. A bypass loop enables the operator to control the pressure and flow-rate in the test sections by the manipulation of control valves V1 and V2. The temperature of the feed solution was kept constant by cold water flowing through the cooling coil. The flow of the cooling water was controlled by a temperature controller (TC) coupled to a solenoid valve (V3) and a thermocouple in the feed tank.

The test rack consisted of 12 test cells connected in series. The permeate from each 0,4 m long cell was returned to the feed tank. Volumetric flasks of various sizes (according to the permeate flow rate) were used for sample collection.

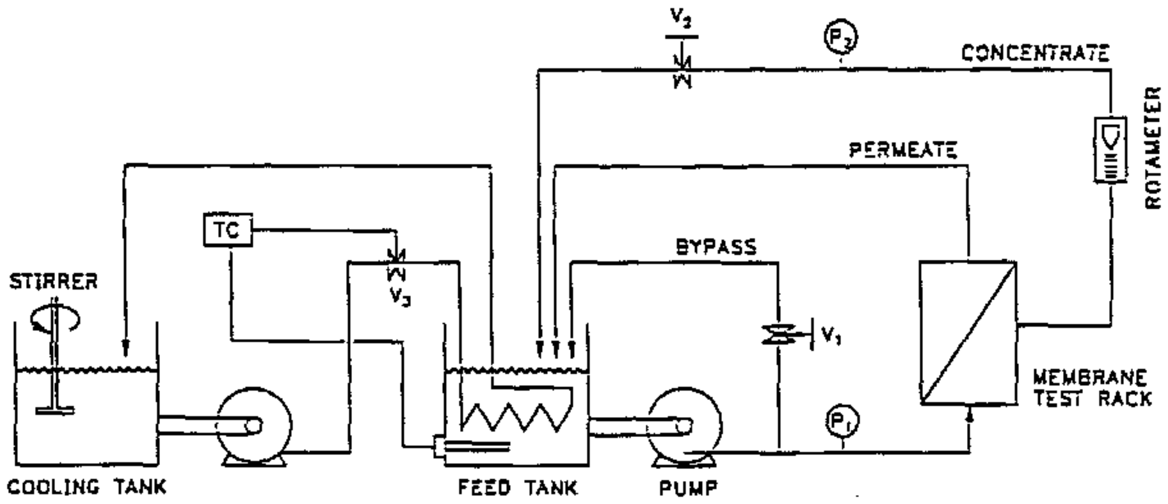


FIGURE 53:
RO testing apparatus

Conductivity measurement

All conductivity measurements were done in a conductivity cell (constant = 0.316 cm) connected to a RADIOMETER COPENHAGEN CDM 83 conductivity meter. Water from a constant-temperature bath (30 °C) was continuously circulated through the cell. The apparatus was calibrated regularly with standard solutions, and conductivity measurements were, where necessary, converted to concentrations by means of calibration curves prepared for this purpose.

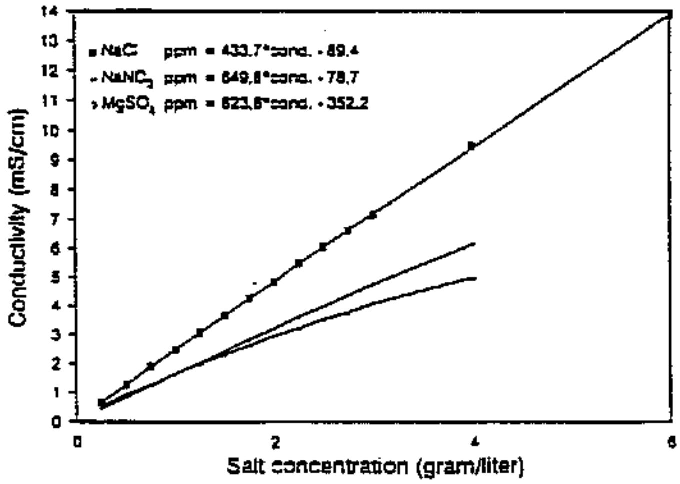


FIGURE 54:
Calibration curves for NaCl, $MgSO_4$, and $NaNO_3$

Experimental procedures

After thorough cleansing and rinsing of the system, membranes were placed in the test cells and a salt solution was prepared by adding a concentrated salt solution to the water in the feed tank. The concentration of the salt in the feed tank was adjusted to the desired constant level by circulating the solution and adding more salt or water as required. The concentration was determined indirectly by conductivity measurement. The operating pressure and flow-rate were then adjusted to the desired levels, and permeate samples were collected at various time intervals.

The permeate flow-rates were determined by the use of a stop-watch and volumetric flasks. The conductivities of the samples were then measured with the conductivity meter, and they were compared with that of the feed sample to evaluate the membranes.

Evaluation criteria

The salt-retention values were calculated by the following equation. Since the relationship between concentration and conductivity of the salt solutions is essentially linear at the levels used in the tests, concentrations can be substituted by conductivities:

$$\text{Retention} \quad = \quad 1 - \frac{\text{Conductivity of the feed}}{\text{Conductivity of the permeate}} \times 100$$

The permeate flow rates (in ml/s) were converted to fluxes (in lmh) by using the surface area of the membrane; thus, for a 0,4 m membrane with a diameter of 13 mm:

$$\text{Flux [lmh]} \quad = \quad \text{Flow rate [ml/s]} \times 220{,}37$$

2.4.3 RESULTS AND DISCUSSION

2.4.3.1 PK Membranes

The effects of several fabrication variables on the RO performances of PK membranes, together with graphic representations have been presented in section 2.3.3.3. (They have been presented there together with other data on insolubilized PVAL membranes.)

2.4.3.2 PKPIP Membranes

These membranes were formed by the deposition of a polyamide membrane onto a $K_2S_2O_8$-crosslinked PVAL membrane. Apart from the influence of the parameters listed below, it was therefore expected that the variables encountered in the preparation of the PVAL base membranes (see 2.3.3.3) would also have an effect on the performance of the PKPIP-type composite membranes. Fabrication variables for fabrication of PKPIP membranes therefore included:

(i) PIP concentration
(ii) Scavenger concentration
(iii) PIP dip time
(iv) PIP drain time
(v) IPC concentration
(vi) IPC dip time
(vii) IPC drain time
(viii) Curing temperature
(ix) Curing time

In the discussion of the influences of fabrication variables on the salt-retention properties of these PKPIP membranes, the effects of variables involved in the preparation of the PK base membranes will be followed by the variables involved in the deposition of the ultra-thin polyamide skin. All the PKPIP membrane were, unless otherwise specified, made according to the following basic variables.

TABLE 23:

Basic conditions adhered to in the production of PKPIP membranes

PARAMETER	VALUE
[PIP]	2 %
[Scavenger](TEA)	1 %
PIP Dip time:	18 hr
PIP Drain time:	24 hr
[IPC]:	1 %
IPC Dip time:	60 s
IPC Drain time:	24 hr
Curing temp.:	80 °C
Curing time:	20 min

(a) Effect of PVAL concentration

When the PK membranes made from solutions containing various concentrations of PVAL (see 2.3.3.3a) were treated further with PIP and IPC, the membrane properties did not show the same general trends as the untreated PVAL membranes. The retention increased minimally and the flux decreased as the PVAL concentration increased from 0,5 to 3,0% (Figs. 55 and 56). Comparison of these figures with Figures 9 and 10 shows that the deposition of the polyamide onto the PVAL membrane resulted in a drastic decrease in flux and a doubling of the NaCl retention. It could therefore be concluded that the polyamide skin determined the diffusion rates of salt and water through the membrane, and that the effect of the PVAL concentration on the performance of PKPIP membranes was negligible.

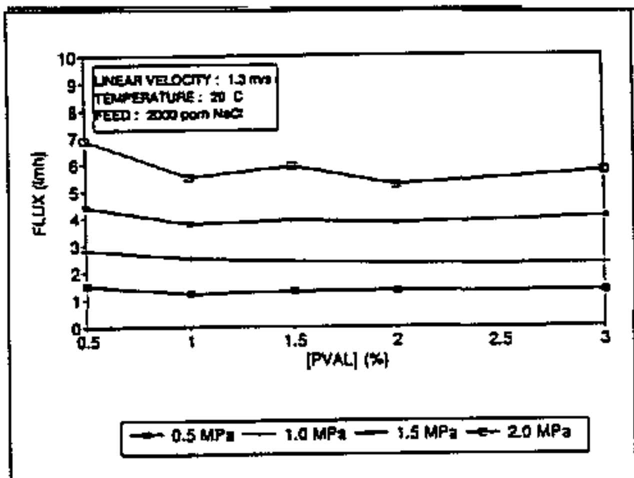


Figure 55:
Effect of PVAL concentration on permeate flux
of PKPIP membranes at different pressures

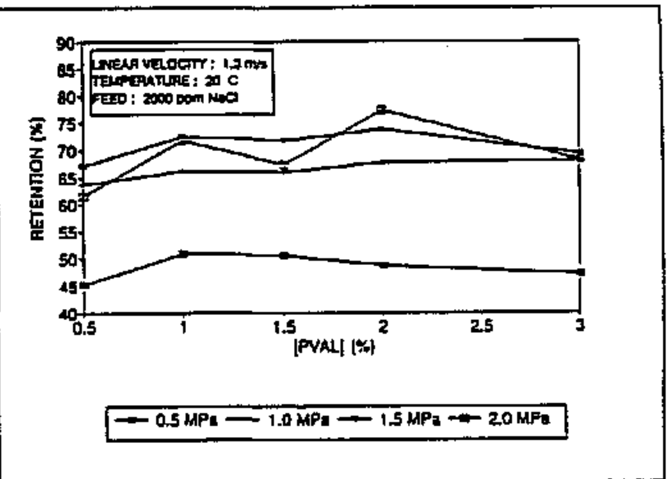


Figure 56:
Effect of PVAL concentration on NaCl retention
of PKPIP membranes at different pressures

(b) Effect of $K_2S_2O_8$ concentration

(i) First reading: *24 h after start-up (Fig. 57 and 58)*

The deposition of the interfacial polyamide resulted in an increase of about 45% in salt retention and a 70% decrease in flux (Percentage change quoted for 2% $K_2S_2O_8$ at 2 MPa). An increase in the $K_2S_2O_8$

concentration resulted in increase in retentions, whereas it had little effect on the permeate fluxes of PKPIP membranes.

(ii) Second reading: 100 h after start-up (Fig. 59 and 60)

When these graphs are compared with those in Figures 57 and 58, it is obvious, despite the irregularities present in some of the graphs, that the performances of the membranes were time-dependent, that is, the retention percentages and flux values changed with the time during which the membranes were operational.

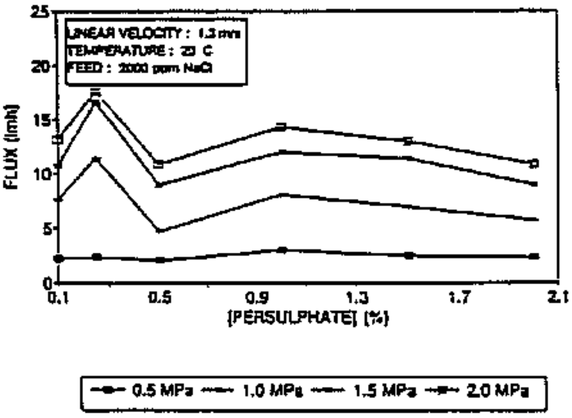


Figure 57:
Effect of persulphate concentration on permeate flux at different pressures. (24 h)

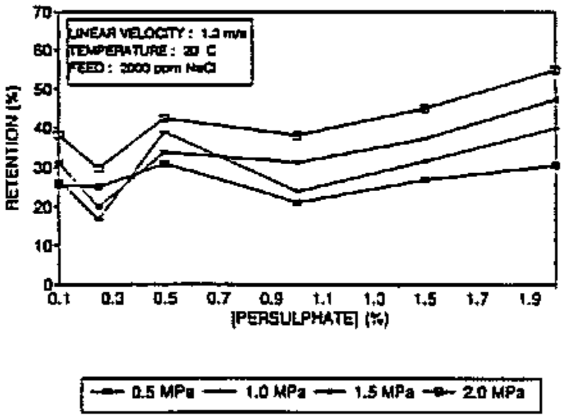


Figure 58:
Effect of persulphate concentration on NaCl retention at different pressures. (24 h)

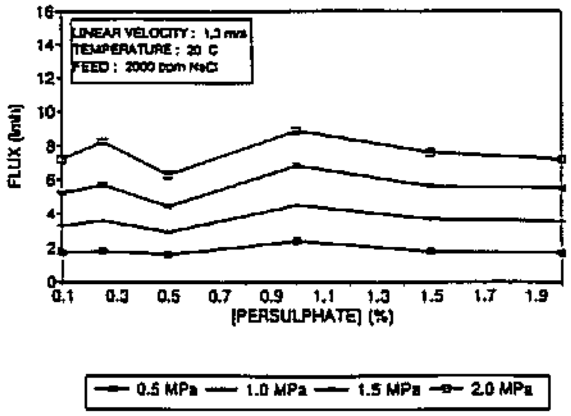


Figure 59:
Effect of persulphate concentration on permeate flux at different pressures. (100 h)

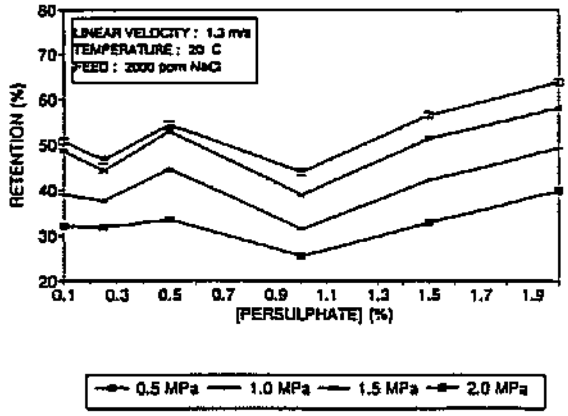


Figure 60:
Effect of persulphate concentration on NaCl retention at different pressures. (100 h)

Table 24 indicates the effect of test time on the RO performance of the PKPIP membranes.

TABLE 24:
Effect of running-time on the performance of PKPIP membranes

Time (hrs.)	Retention (%)	Flux (lmh)
24	55	18
100	64	9

The increase in retention and decrease in flux with time can be attributed to the compaction of the swollen PVAL gel layer or by membrane fouling by the penetration of the gel-layer into the pores.

(c) Effect of PIP concentration

High concentrations of PIP (10 - 20%) led to the formation of thick brittle polyamide membranes after reaction with IPC. These membranes did not adhere to the PVAL very well and tended to peel off when they were removed from the IPC solution. A PIP concentration of 2% was subsequently used for all the PKPIP membranes described. Further investigations into the PKPIP membranes were discontinued due to their low fluxes.

(d) Effect of scavenger concentration

Triethylamine (TEA) was added to PIP solutions at a concentration of 1% to act as an acid scavenger in the condensation reaction of PIP with IPC to neutralize the HCl formed. NaOH could also be used for this purpose.

(e) Effect of PIP dip- and drain-times

The PVAL membranes were immersed in the PIP solution for approximately 24 h to ensure the thorough wetting of the membrane and subsequently drained for 2 - 3 days. The draining was done at 100% relative humidity in a plastic bag containing a little water to prevent the membranes from drying out completely. The long draining time was used to prevent the formation of a thick membrane that would reduce the permeate flux.

(f) Effect of IPC concentration

The IPC concentration of 1% in hexane was used for the fabrication of all the PKPIP membranes referred to in this report.

(g) Effect of IPC dip time

PVAL membranes (cured at 80°C) were treated with PIP, drained and immersed in a 1% IPC solution for a time ranging from 60 to 300 s. These composite membranes were evaluated at pressures of 0,5 to 2 MPa on feed solutions containing 2 000 ppm NaCl and 1 000 ppm $MgSO_4$, respectively. The results in Figures 61 and 62 show that the flux decreased and the retention was almost static with increase in IPC dip time. These phenomena can be ascribed to the formation of thicker polyamide layers as the treatment time was increased.

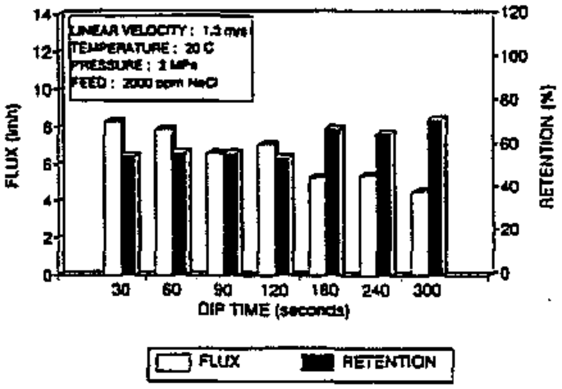


Figure 61:
Effect of IPC dip time membrane performance

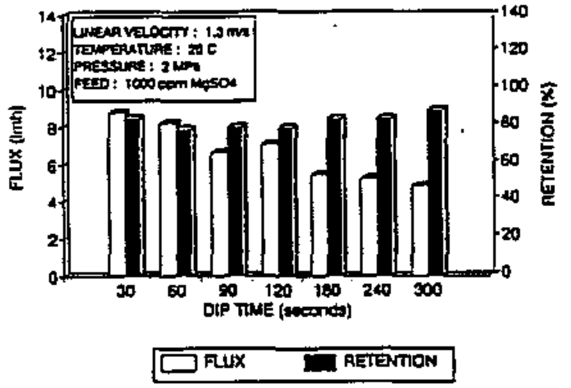


Figure 62:
Effect of IPC dip time membrane performance

(h) Effect of IPC drain time

The membranes were air-dried at room temperature for 1-2 days to eliminate excess solvent.

(i) Effect of curing time and temperature

Twelve membranes were treated in the usual manner up to the draining of the PIP solution; six of which were treated with IPC for 60 s (Figures 63 and 65) and six for 300 s (Figures 64 and 66). After air-drying they were cured for 20 min at temperatures ranging from 60 - 110 °C. In general, the permeate flux decreased with increase in curing temperature, as the higher temperature produced membranes of higher crosslink density.

The opposite trend was expected for the retention, that is, an increase in retention with an increase in curing temperature. As Figures 63 and 64 show, however, the general trend was a decrease in NaCl retention as the temperature is increased from 60 to 110 °C.

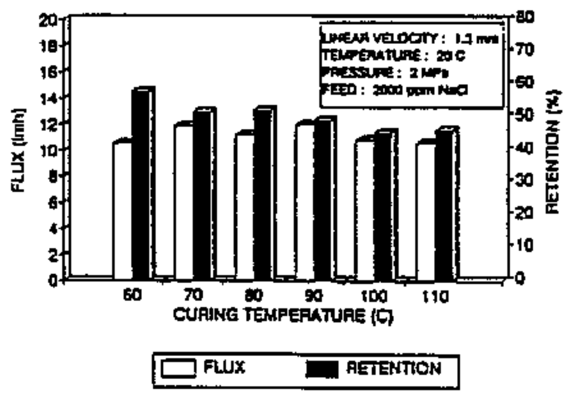


Figure 63:
Effect of curing time on membrane performance.
(IPC dip time = 60 s)

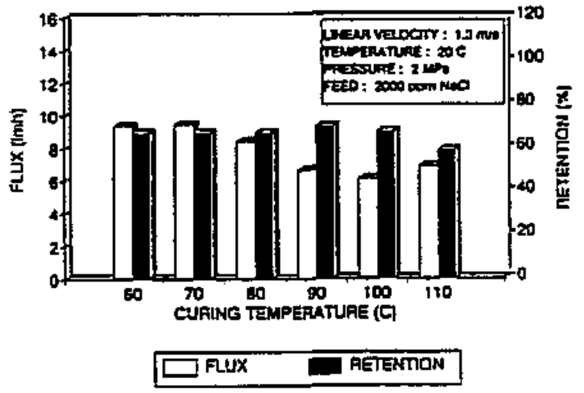


Figure 64:
Effect of curing time on membrane performance.
(IPC dip time = 300 s)

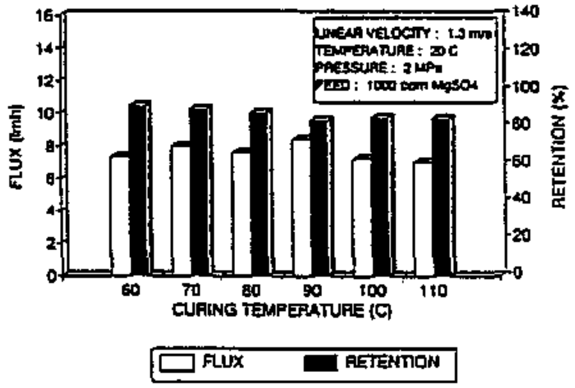


Figure 65:
Effect of curing time on membrane performance.
(IPC dip time = 60 s)

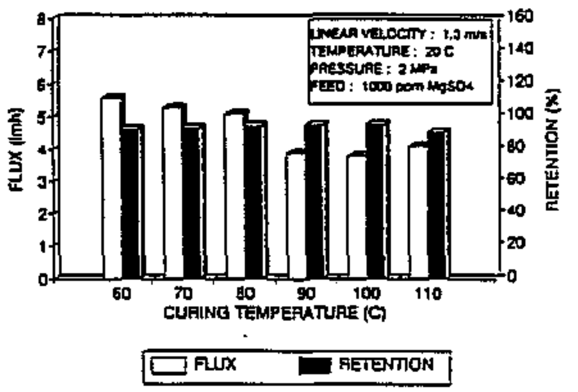


Figure 66:
Effect of curing time on membrane performance.
(IPC dip time = 300 s)

2.4.3.3 PPA membranes

The parameters expected to influence the RO performance of the PPA membranes were:

(i) PVAL concentration
(ii) Amine concentration
(iii) Amine type
(iv) Scavenger concentration
(v) PVAL/Amine dip time
(vi) PVAL/Amine drain time
(vii) Diacid chloride concentration
(viii) Diacid chloride dip time
(ix) Diacid chloride drain time
(x) Curing temperature
(xi) Curing time

(a) PPIP membranes

Instead of determining the effects of all the abovementioned parameters on membrane performance, a new approach was decided upon, namely, to produce membranes with the desired properties in a shorter time. Various aqueous and organic solutions were prepared (shown in Table 25), and membranes were made according to the conditions listed in Table 26. These parameters were considered to be a good starting point, and were decided upon after consultation with fellow membrane-researchers at this Institute. Table 25 below shows that the aqueous solution used for the fabrication of PPIP membranes contained mainly PVAL and PIP, but in two of the examples other multifunctional amines (TAB and CPA) were added in small quantities. The organic phases consisted of either IPC or TMC in hexane.

The membranes made from all possible combinations of the solutions in Table 25 were coded according to the solutions used in each case, for example, N1X1 refers to a membrane made with solutions N1 and X1. As there were four aqueous solutions and three organic crosslinking solutions, a total of twelve variations of PPIP membranes were made. For all PPIP membranes codes containing an N, i.e. - N1X1 - N4X3, the manufacturing conditions were as follows:

TABLE 25:
Aqueous and organic phases for the fabrication of PPIP membranes

AQUEOUS PHASE			ORGANIC PHASE		
CODE	CONTENTS	QUANTITY (m%)	CODE	CONTENTS	QUANTITY (mass%)
N1 or M1	PVAL-B	0.25	X1	IPC	1.00
	PIP	0.25		HEXANE	99.00
	NaOH	0.50			
	H_2O	99.00			
N2 or M2	PVAL-B	0.50	X2	TMC	1.00
	PIP	0.50		HEXANE	99.00
	NaOH	0.95			
	H_2O	98.05			
N3 or M3	PVAL-B	0.50	X3	TMC	2.00
	PIP	0.45		HEXANE	98.00
	TAB	0.05			
	NaOH	0.95			
	H_2O	98.05			
N4 or M4	PVAL-B	0.50			
	PIP	0.45			
	CPA	0.05			
	NaOH	0.95			
	H_2O	98.05			

TABLE 26:
Basic conditions adhered to in the production of PPIP membranes, designated NX

PARAMETER	VALUE
Pre-drain:	5 min
Aqueous dip:	5 min
Post drain:	15 min
Organic dip:	1 min
Air dry:	15 min
Oven temperature:	110 °C
Curing time:	10 min

These conditions were later partly revised to those listed in Table 27, and six membranes were made according to the revised conditions. All PPIP membranes made by using the revised conditions are coded with an M instead of an N, for example, M1X1 instead of N1X1.

TABLE 27:
Basic conditions adhered to in the production of PPIP membranes, designated MX

PARAMETER	VALUE
Pre-drain:	10 min
Aqueous dip:	10 min
Post drain:	15 min
Organic dip:	3 min
Air dry:	15 min
Oven temperature:	110 °C
Curing time:	10 min

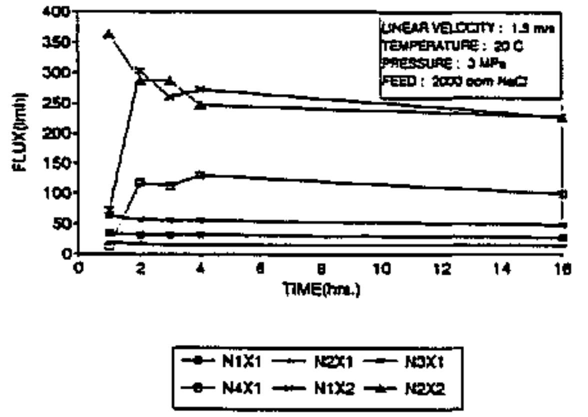
The following types of PPIP membranes were made, as shown in Table 28:

TABLE 28:
List of PPIP membrane types made and tested

N1X1 N2X1 N3X1 N4X1	N1X2 N2X2 N3X2 N4X2	N1X3 N2X3 N3X3 N4X3
M1X1 M2X1 M3X1		M1X3 M2X3 M3X3

Two membranes of each of the types mentioned above were produced for evaluation. Figures 67 - 72 depict the salt-retention properties of the different types of PPIP membranes. The salt-retention properties of the six membranes shown in Figures 67 and 68 clearly indicate that the membranes made from combinations N4X1, N1X2 and N2X2 had very poor salt retentions, with corresponding high permeate fluxes. The retention of salt by membrane N3X1 was only slightly higher, at approximately 35%, while membranes N1X1 and N2X1 showed retentions of above 60% and 80%, respectively. The retentions of the other six membranes in the original series (Figures 69 and 70) were very low. It was therefore concluded that the use of crosslinking solution X1 produced membranes superior to those made from crosslinking solutions X2 and X3 and that of the four aqueous solutions, the use of solution N4 (containing PIP and CPA) invariably led to the production of membranes with poor salt retentions.

The results obtained from the six membranes made according to the revised conditions from combinations of solutions M1 and M3, and X1 and X3 are shown in Figures 71 and 72. When the results in Figure 72 are compared with those in Figure 68, it can be seen that the revision of the fabrication conditions had a very small effect on the performance of the membranes made from solutions N1 and X1. The change of conditions did, however, improve the salt-retention by membranes made from solutions N2 and X1, as well as that of membranes made from solutions N1 and X3.



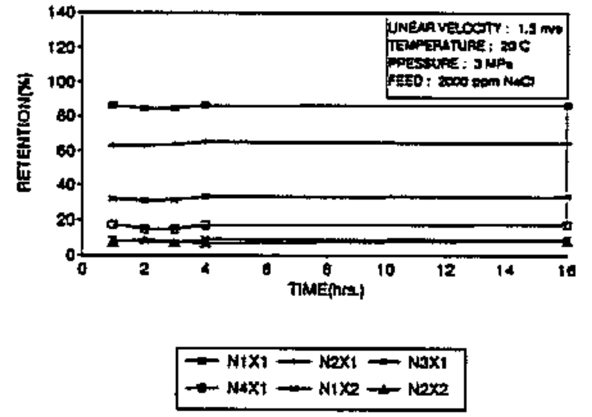
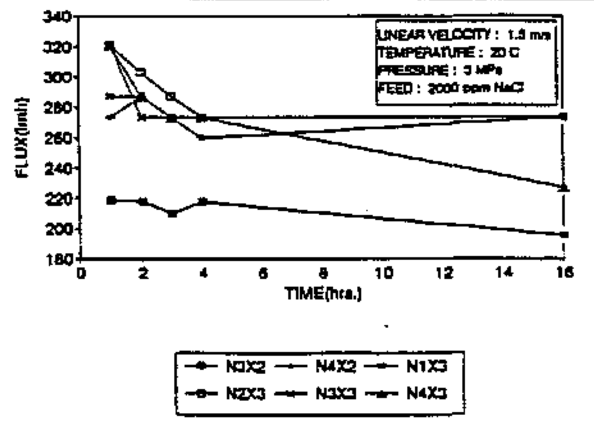


Figure 67:
Effect of production method on permeate flux

Figure 68:
Effect of production method on NaCl retention



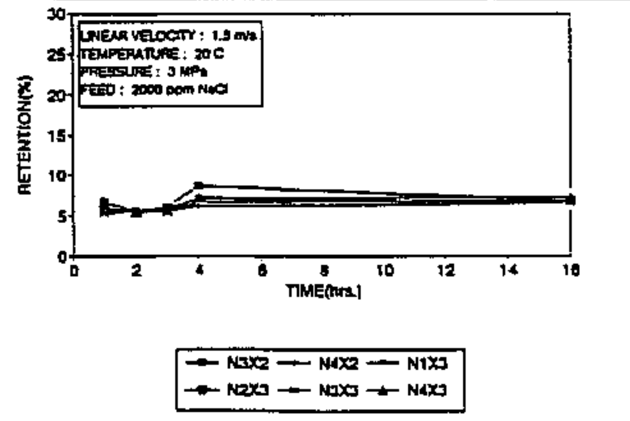


Figure 69:
Effect of production method on permeate flux

Figure 70:
Effect of production method on NaCl retention

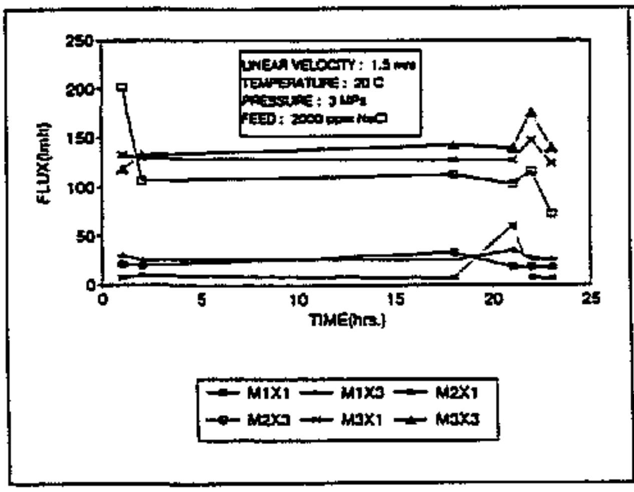


Figure 71:
Effect of production method on permeate flux

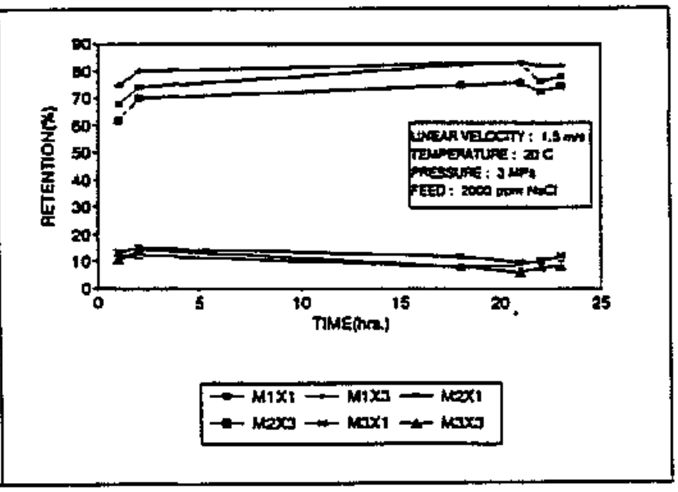


Figure 72:
Effect of production method on NaCl retention

(b) PPDAA MEMBRANES

In the preparation of PVAL/PIP membranes an acid scavenger was added to the aqueous solutions from which the membranes were made. In the preparation of PPDAA membranes, however, the addition of NaOH or TEA to the PVAL/PDAA mixture resulted in the precipitation of the polydiallylammonium phosphate. The addition of TEA to the IPC solution also caused the precipitation of the IPC. Separate solutions of NaOH and TEA were therefore made in water and hexane, respectively, and these solutions were used at different stages of membrane formation, as shown in Table 29. The procedures listed in Table 30 were followed as a trial run in the making of membranes from PDAAP, and need to be repeated and modified in future experiments to improve the process. The initial results of membranes tested on a 2 000 ppm NaCl solution at 2 MPa are given in Table 31.

TABLE 29:
Solutions used in the production of PVAL/PDAA membranes

SOLUTION CODE	CONTENTS	QUANTITY(m%)
A	PVAL PDAAP H_2O	0.25 0.25 99.50
B	NaOH H_2O	0.50 99.50
C	IPC HEXANE	1.00 99.00
D	TEA HEXANE	0.50 99.50

TABLE 30::
Procedures for PVAL/PDAA membrane formation

MEMBRANE CODE	PROCEDURE	TIME (min)
D1	Pre-drain	3.0
	Dip solution A	5.0
	Drain	2.0
	Dip solution B	0.5
	Drain	5.0
	Dip solution C	1.0
	Drain	5.0
	Cure (100 °C)	10.0
D2	Pre-drain	3.0
	Dip solution A	5.0
	Drain	5.0
	Dip solution C	1.0
	Drain	2.0
	Dip solution E	0.5
	Drain	5.0
	Cure (100 °C)	10.0
D3	Pre-drain	3.0
	Dip solution A	5.0
	Drain	5.0
	Dip solution E	0.5
	Drain	2.0
	Dip solution C	1.0
	Drain	5.0
	Cure (100 °C)	10.0

TABLE 31:
Membrane performance results of PVAL/PDAA membranes

MEMBRANE CODE	RETENTION (%)	FLUX (lmh)
D1	22.1	49.2
D2	31.9	15.3
D3	46.0	19.4

2.4.4 TREATMENT OF INDUSTRIAL WASTEWATER

2.4.4.1 Introduction

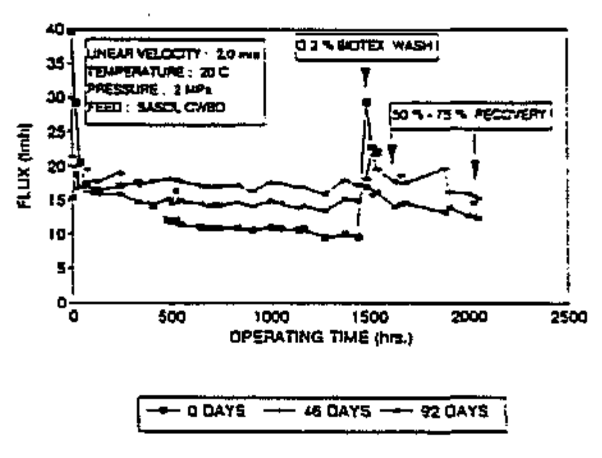
To date, all the membranes described have been tested on synthetic brackish water made up in the laboratory. The solutions consisted of a single salt dissolved in RO-treated water, and contained no other inorganic or organic impurities. PK and PPA type membranes were then also evaluated on a "genuine" industrial effluent: cooling-water blowdown (CWBD) from the SASOL plant in Secunda. Table 32 gives an indication of the properties of the CWBD.

TABLE 32:
SASOL CWBD analysis

PROPERTY	QUANTITY	PROPERTY	QUANTITY
$[Cl^-]$ (mg/l)	350 to 500	$[K^+]$ (mg/l)	100 to 130
$[F^-]$ (mg/l)	400 to 500	$[Na^+]$ (mg/l)	500 to 900
$[SO_4^{2-}]$ (mg/l)	1000 to 1200	$[Ca^{2+}]$ (mg/l)	20 to 30
$[PO_4^{3-}]$ (mg/l)	10 to 30	[Fe] (mg/l)	10 to 20
COD (mg/l)	2600 to 3100	$[SiO_2]$ (mg/l)	150 to 170
Turbidity	60 to 100		

2.4.4.2 "In-house" - first test

This test was performed at the Institute for Polymer Science. PK-type membranes were made from 3% PVAL solutions containing 1,5% $K_2S_2O_8$ after various maturation times; three membranes were made from PVAL-A and three from PVAL-B. The conductivity, retention and flux data are shown in Figures 73 - 76. The retention properties of the membranes were fairly constant over the total operating time, and showed only a slight decrease at high recoveries (Figures 74 and 76). The wash at approximately 1 500 h had very little effect on the retention. It was evident that membranes produced from solutions containing the PVAL with the lower molecular mass (PVAL-A) needed more maturation to produce retentions comparable to those made from PVAL-B. It was also clear from these graphs that the retention increased with increased maturation, irrespective of the molecular mass of the PVAL.



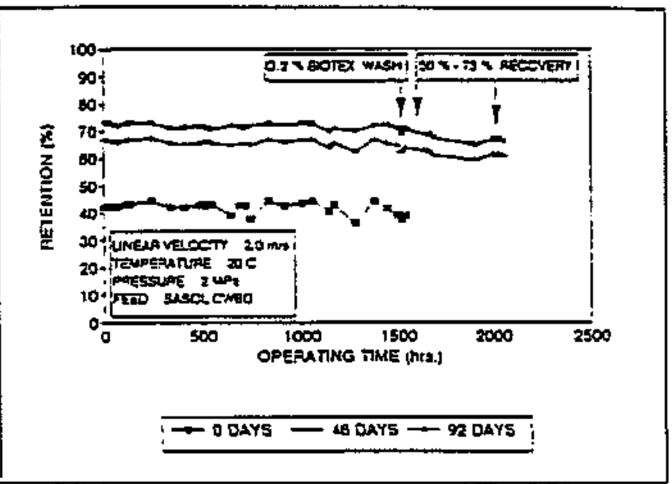
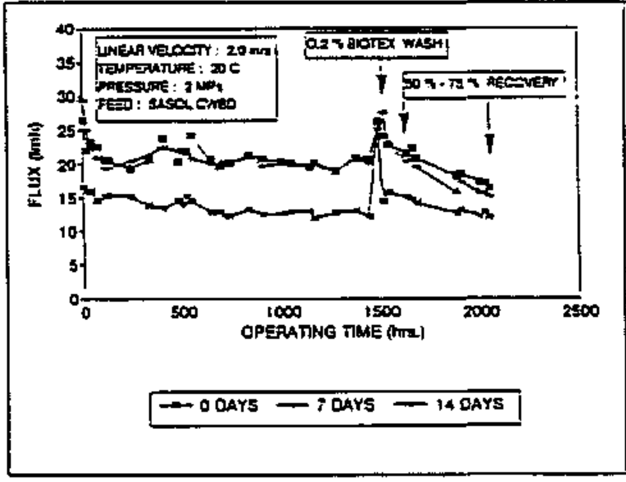


Figure 73:
Permeate fluxes of PK membranes made from
PVAL-A at various stages of maturation

Figure 74:
Conductivity retentions of PK membranes made from
PVAL-A at various stages of maturation



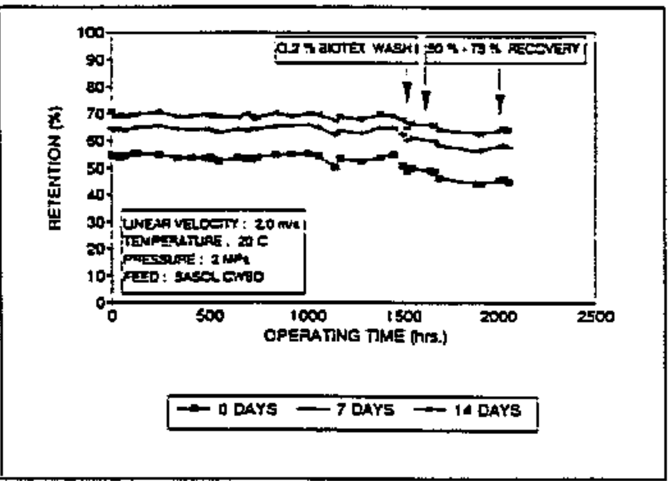


Figure 75:
Permeate fluxes of PK membranes made from
PVAL-B at various stages of maturation

Figure 76:
Conductivity retentions of PK membranes made
from PVAL-B at various stages of maturation

The permeate fluxes (Figures 73 and 75) showed an initial decrease whereafter equilibrium values, apparently, were reached. The enzyme active soap wash lead to a marked increase in the permeate flux rate, whereafter the fluxes again decreased rapidly to the equilibrium values. The initial flux decrease was highest for unmatured membranes, which confirmed the stabilization effect of solution maturation on the membrane properties. Figure 77 shows the log flux/log time plot used to determine the flux decline index of the membranes made from PVAL-A according to the following formula [2].

$$F_t = Ktm \qquad (1)$$

where F_t is the flux at time t, K is a constant, and m is the log-log flux decline index or fouling factor. Equation (1) predicts that a log-log plot of flux versus time will yield a straight line with a negative slope m. The constant K is generally taken to be the initial flux (F_0), and therefore the flux decline index can be expressed as

$$m = \log(F_t/F_0)/\log(t/t_0) \quad (2)$$

A value of m = -0,10 corresponds to a flux of about 55% of the original flux after one year, and a value of m = -0,03 corresponds to a 17% decrease in flux over the same time period.

When the index for the unmatured membrane (m = -0,23) was compared with that of the matured membranes (m = -0,05) it was clear that maturation of the PVAL solution enhanced the fouling resistance of the PK-type membranes.

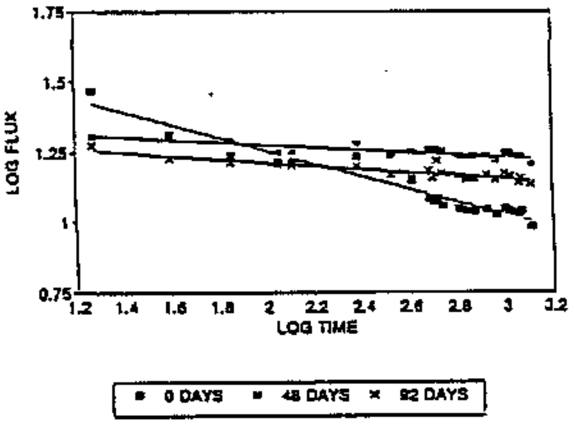


FIGURE 77:
Log-log plot of flux versus time for PK membranes made from
a solution containing PVAL-A

2.4.4.3 "Onsite" - second test

Mobile RO test equipment was set up at SASOL for the "on-site" evaluation of PK membranes . Five PK membranes, made from low- and high-molecular-mass PVAL at different stages of maturation (See Table 33), were evaluated on CWBD, and the results were compared with those obtained in tests at this Institute. A cellulose acetate membrane (obtained from MEMBRATEK) was also placed in one of the six test cells on the RO rig, as comparison.

TABLE 33:
Membranes tested on CWBD

TEST CELL	MEMBRANE	PVAL Mol.Mass	MATURATION (days)
1	CA		
2	PK	72 000	92
3	PK	15 000	46
4	PK	15 000	92
5	PK	72 000	14
6	PK	72 000	21

Figures 78 and 79 show the permeate flux and conductivity retentions of these membranes. It should be noted that the temperature of the feed solution fluctuated considerably over the test period because of the unavailability of temperature controllers. Tap water was, however, passed continuously through a cooling coil in the feed tank to control the temperature to some degree.

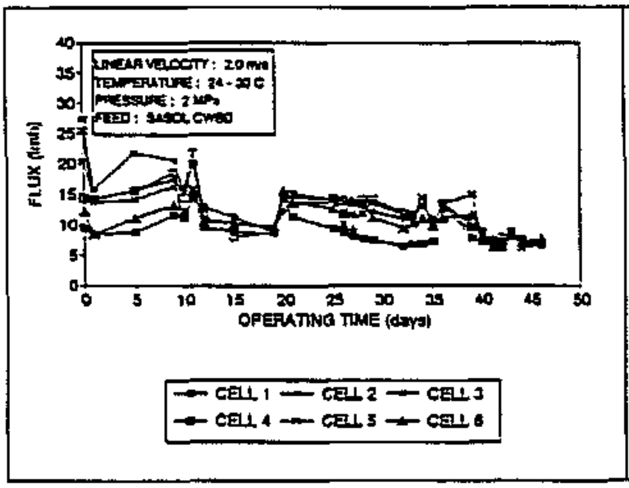


Figure 78:
Permeate fluxes of CA and PK membranes made at various stages of maturation

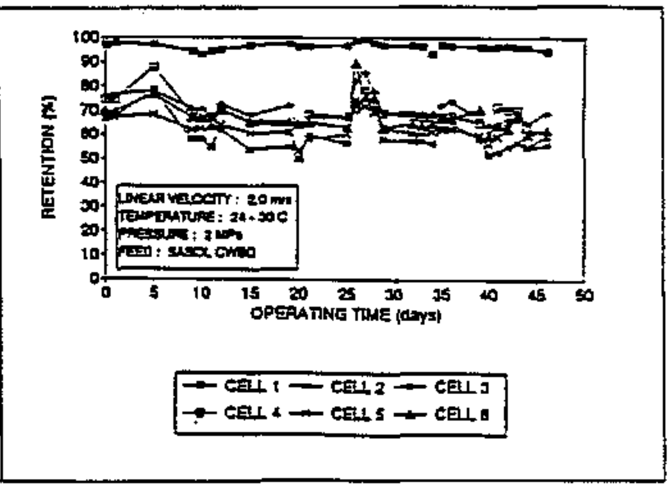


Figure 79:
Conductivity retentions of CA and PK membranes made at various stages of maturation

The conductivity retentions of the PK-type membranes ranged from 50% to 80%, while the CA membrane showed a much higher retention exceeding 95% with no apparent deterioration over the test period. Although the initial fluxes of the PK membranes were higher than that of the CA membrane, all the membranes exhibited similar fluxes (5-10 lmh) after 40 h. The fluxes of all the PK membranes evaluated in this test were appreciably lower than those obtained from similar membranes in the first test (2.4.4.2). This shows that samples of industrial effluents are often not representative of the bulk stream at the source, and that experimental membranes should be tested as close to the source of the effluent as possible.

The colour retention and the retentions of specific ions were also calculated after more detailed analyses of the permeates by the SASOL staff (Figures 80 through 86).

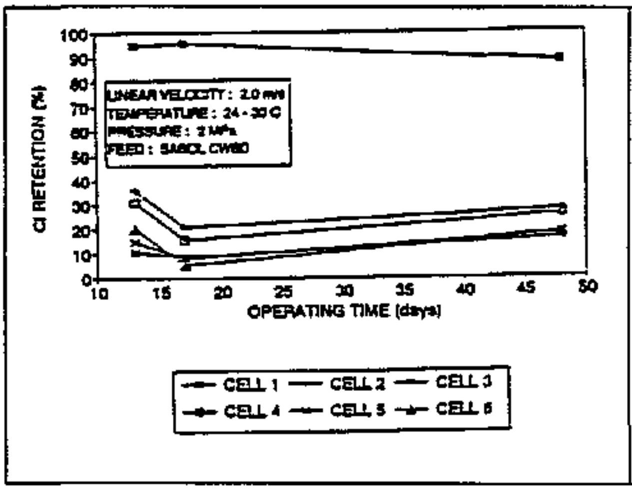


Figure 80:
Chloride retentions of PK membranes made
at various stages of maturation

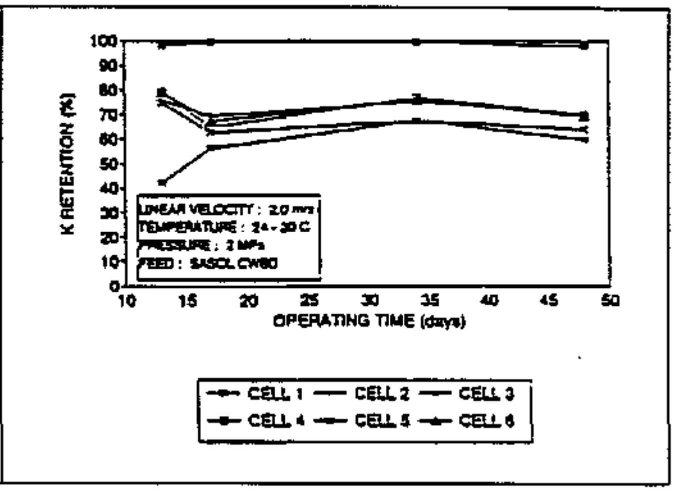
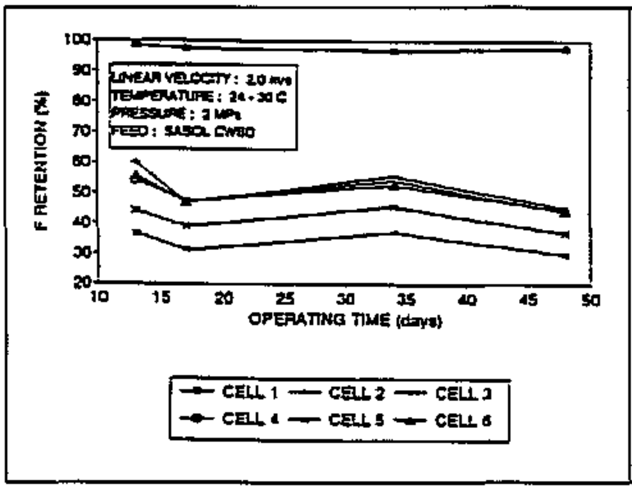


Figure 81:
Potassium retentions of PK membranes made
at various stages of maturation



, Figure 82:
Fluoride retentions of PK membranes made
at various stages of maturation

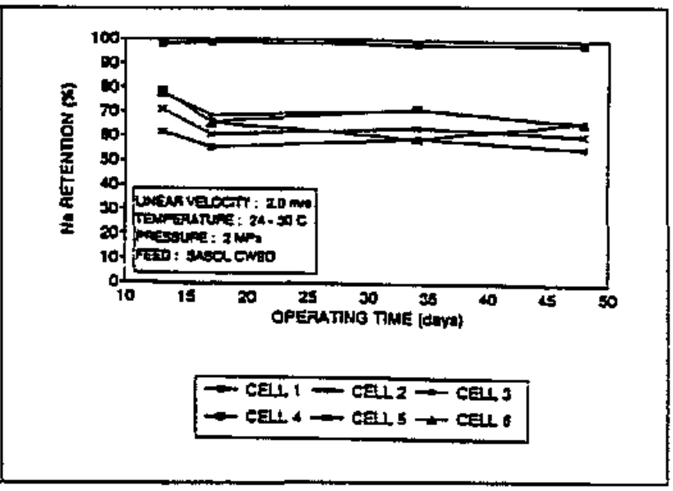


Figure 83:
Sodium retentions of PK membranes made
at various stages of maturation

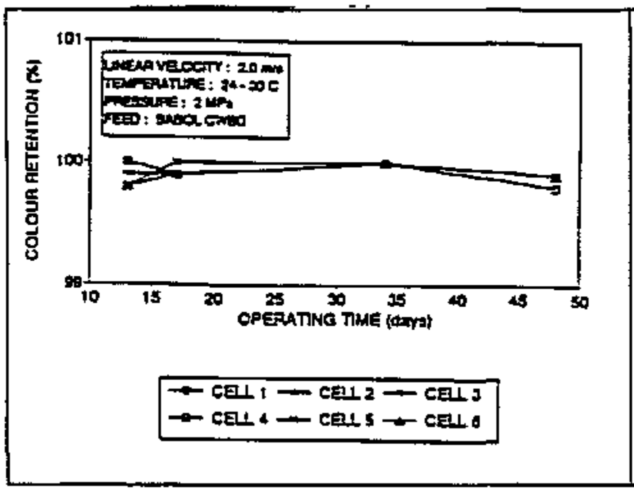


Figure 84:
Colour retentions of PK membranes made
at various stages of maturation

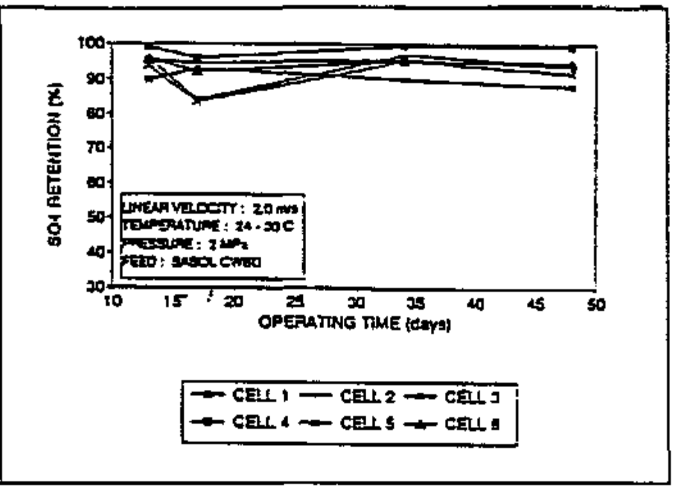
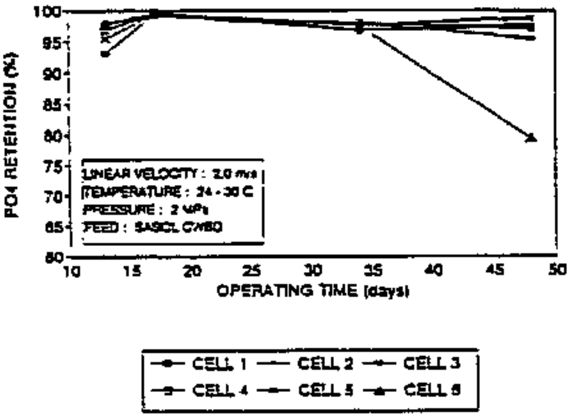


Figure 85:
Sulphate retentions of PK membranes made
at various stages of maturation



<u>FIGURE 86</u>:
Phosphate retentions of PK membranes, made at various stages of maturation

The retention of monovalent cations (K+ and Na+) by the PK membranes varied from 60-70%, whereas the monovalent anions were rejected at much lower values; ranging from 10-40% for chloride and 30-60% for fluoride. The retention of sulphate ions was slightly lower than that observed with CA membranes, whereas the phosphate retention was similar to that obtained from the CA membranes.

2.4.4.4 Third test

On a second visit to SASOL, three new experimental membranes were tested on the CWBD. The first was a PPIP (N1X1) membrane, the fabrication of which has been described previously (section 2.4.3.3). Two further membranes, namely, CAMOH and CAMPIP, the preparation of which have been described in section 4 and Addendum 4), were also tested. Figures 87 and 88 show the permeate fluxes and also conductivity retentions obtained from these membranes. For the first 100 h of operation the system was run at 0% recovery, after which the recovery was increased to 20%, 40% and 75%.

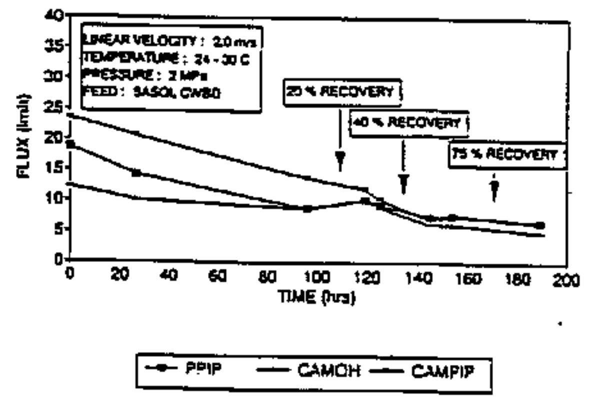


Figure 87:
Permeate fluxes of PPIP, CAMOH and CAMPIP membranes

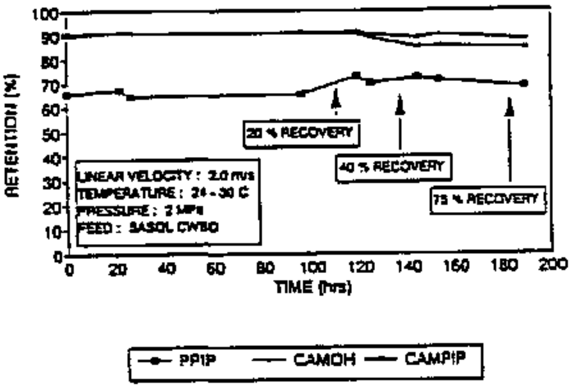


Figure 88:
Conductivity retentions of PPIP, CAMOH and CAMPIP membranes

Although the initial fluxes of the membranes differed substantially, the values were very similar at recoveries greater than 20%. The conductivity retentions of the CAMOH and CAMPIP membranes averaged at approximately 90% for the first 100 h of operation, and decreased only slightly to 85% at high recoveries. The initial retention of the PPIP membrane was considerably lower at about 65%, and showed a slight increase to above 70% with greater recoveries.

2.4.5 CONCLUSIONS

1. This study has resulted in an overall appreciation of the many variables pertaining to the formation of nanofiltration and reverse osmosis membranes from polyvinyl alcohol (PVAL) and amine-modified PVAL. Various formulas for the casting membranes were investigated and membranes tested.

2 These membranes were evaluated on synthetic and real effluents to study their performance and fouling characteristics: Tests conducted on the $K_2S_2O_8$ crosslinked PVAL membranes with an industrial effluent showed that the log-log flux decline index decreased considerably with increased maturation of the PVAL/$K_2S_2O_8$ solutions. This again showed the important role that solution maturation plays in the production of tolerant PVAL/$K_2S_2O_8$ membranes.

3. The deposition of an ultra-thin polypiperazine isophthalamide skin on the surface of the insolubilized PVAL sub-layer resulted in increased salt retention, but not without a decrease in the permeate flux. Typical results are given below:

80% retention; < 240 lmh (10 lmh)	2000 ppm NaCl; 2 MPa; 20°C; 1,3 m/s
75% retention; < 240 lmh (10 lmh)	1000 ppm $MgSO_4$; 2 MPa; 20°C; 1,3 m/s

4. Composite ultra-thin film (UTF) membranes could also be made without the insolubilization of the PVAL prior to the deposition of the polyamide skin. This could be achieved by the interfacial reaction of a mixture of PVAL and an amine (in aqueous solution) with a suitable multifunctional acid chloride (in an organic solvent). The best RO performance results were obtained from membranes prepared by the reaction of an aqueous solution containing 0,25% PVAL, 0,25% piperazine (PIP) and 0.5% NaOH with a 1% solution of isophthaloyl chloride in hexane:

   >80% retention; 960 lmh (40 lmh) flux   2000 ppm NaCl; 3 MPa; 20°C; 1,5 m/s

   Poorer results were obtained when mixtures of monomeric tetrafunctional amines and PIP were used, and when the trifunctional acid chloride trimesoyl chloride (TMC) was used as crosslinking agent.

   A novel approach involving the use of polydiallylamine (PDAA) instead of PIP led to the production of membranes with poorer retentions, probably due to the fact that membranes had to be made by a modified dip-coating procedure.

5. In order to subject these PVAL-based membranes to more thorough testing, they were installed into modules and tested. This resulted in a decrease in the salt retentions of the composite UTF membranes (PVAL/PIP/IPC). This was subsequently found to be due to the

failure of only a few of the membrane tubes in the module; these tubes were probably damaged during module assembly.

6. In the continued search for different ways to produce efficient PVAL/PA membranes, the cyclopolymer PDAA was selected for use; it possesses a cyclic structure and secondary amine functionality. Various ways of preparing the polymer were investigated and it was found that the anhydrous hydrochlorination of diallylamine (DAA) in acetone resulted in much higher yields than when ethanol was used as a solvent. It was also found that the polymerization of DAA in excess H_3PO_4 with low temperature redox initiation ($K_2S_2O_8/TiCl_3$) is preferable to the high temperature $K_2S_2O_8/Na_2S_2O_3$ initiation of diallylammonium chloride.

7. Initial membranes made from PDAA did not show any improvement in RO properties. Nonetheless, the fact that adequate membranes could be made, even though a lenghthy three-step coating was necessitated, has opened up many possibilities for the use of this polymer in creating tolerant membranes.

Suggested recommendations

1. Polyamide membranes should be made from PDAA and IPC (with or without other additives) and compared to those made with PVAL/PDAA/IPC.

2. Various copolymers of DAA should be prepared and used for the production of composite membranes. Special attention needs to be placed on solubility promotion by the co-monomers.

3. The reactions of $K_2S_2O_8$ with PVAL should be further investigated with the use of solid state NMR and model compound studies to clarify the effect of solution maturation time on RO membrane performance.

4. Research into the use of substrates with higher porosity is necessary if high fluxes are to be obtained from thin PVAL coatings.

5. Further tolerance and chemical stability tests on membranes, or model compounds similar to those expected on the membrane surface, would be an advisable part of future studies involving PDAL-based membranes.

2.4.6 REFERENCES

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PART B

3. RO MEMBRANES FROM AMINE-CONTAINING MEMBRANES PRECURSORS

3.1 POLYVINYLALCOHOL-CO-VINYL P-AMINOPHENYLETHER RO MEMBRANES

3.1.1 INTRODUCTION AND OBJECTIVES

The aim of this investigation was to make a contribution to the development of polyvinyl alcohol RO membranes. To date, numerous techniques have been used to fabricate RO membranes from polyvinyl alcohol: such as cross-linking by heat and radiation treatment or treatment with organic compounds (see section 2.2). Excellent RO performances were reported for membranes which were made by coating a porous polysulphone support with an aqueous solution of polyvinyl alcohol and an amino compound containing two or more amino groups (e.g. piperazine) followed by an interfacial polymerization reaction with an crosslinking agent containing amino and hydroxy functionality (NITTO membranes, see section 2.2). In this study membranes were made from a precursor of modified polyvinyl alcohol: a copolymer containing units of vinyl alcohol and vinyl p-aminophenylether, rather than using polyvinyl alcohol and an amino compound separately. Phenylethers are chemically very stable compounds and amine functionality was incorporated in this copolymer of polyvinyl alcohol by a strong bond.

3.1.2 LITERATURE SURVEY

An extensive literature survey was completed as part of a M.Sc.-thesis by Heloïse Gerber (thesis in preparation).

3.1.3 MATERIALS AND METHODS

3.1.3.1 Preparation of modified polyvinyl alcohol

Polyvinyl alcohol-co-vinyl p-aminophenylether (PVACVAPE) was prepared in a three-step synthesis. Firstly, the hydroxyl group of PVAL was converted into a good leaving group by the formation of p-toluenesulphonylesters (tosylester). Secondly, the ether bond was formed by nucleophillic substitution of the tosylester by a phenolate group, sodium p-acetamidophenolate. Direct etherfication of p-aminophenol was not possible, because both N-alkylation and O-alkylation would have occurred. To ensure that only O-alkylation took place, the amine was protected beforehand by acetylation. The acetamide was then converted back to the amide by acid hydrolysis. ^{1}H-NMR spectroscopy was used to characterize the compounds.

Step 1: Preparation of a p-Toluenesulphonylester of PVAL

The degree of hydrolysis of the PVAL used was 86 - 89% and the MM = 15 000.

PVAL (11 g, 0,25 mole) was swollen in anhydrous pyridine (125 ml), at 100°C for 3 h. After cooling to 0°C, p-toluenesulphonyl chloride (47,66 g; 0,25 mole), dissolved in anhydrous pyridine (250 ml) was added while the temperature was kept below 5°C. The reaction mixture was stirred for 4 h at 0°C to 5°C and then stored in a refrigerator (0° - 5°C) for the required reaction time. Reaction times of 68,20, 16,8 and 4 h were used to obtain different degrees of substitution.

An equal volume of acetone was added and the polymer was precipitated in ice-cold water. The white fibrous polymer was filtered and washed with 6% HCl (100 ml) to remove the traces of pyridine and then washed with water. The product was dissolved in acetone and reprecipitated from an aqueous solution of 6% NaOH (100 ml) to remove the excess p-toluenesulphonyl chloride. The polymer was then filtered, washed twice with water, air dried at room temperature and finally dried over silica gel in a vacuum desiccator at room temperature for 24 h. Phosphorous pentoxide could also be used to dry the product

% Tosylation after 20 h reaction time, as determined by ^{1}H-NMR, was 37,14% and the % yield was 90,2%.

Step 2: Preparation of p-Acetamideophenylether of PVAL

All the syntheses of p-acetamidophenylethers of PVAL were carried out in an oxygen-free atmosphere. Argon gas was used to displace oxygen.

Experiment 1:

In a round-bottom flask, the tosylether of PVAL (2,4 g; 8,4 mmole) was swollen in methylethylketone (MEK) (25 ml), for 1 h at 80°C. To this solution p-acetamideophenol (3,8 g; 25 mmole), an excess of powdered anhydrous K_2CO_3 (5 g; 36 mmole) and an additional volume of MEK (15 ml) were added. The reaction mixture was stirred under reflux at 80°C for 6 h. Most of the product precipitated in MEK and filtration removed not only the K_2CO_3, but also the product. The ether was therefore isolated by washing the precipitate with water, followed by filtration. The original filtrate contained some of the product, but mostly uncreated p-acetamidiphenol. p-Acetamidoether of PVAL in the filtrate was isolated by evaporation of the solvent and then by precipitation of the residue in water. The product was washed with an aqueous solution of 6% NaOH (50 ml) to remove the unreacted p-acetamidophenol.

% Substitution of the p-toluenesulphonylester (37,1%, tosylated PVAL) by p-acetamidophenol, as determined by ^{1}H-NMR spectroscopy, was 73,0% and the % yield was 43,7%.

Experiment 2:

p-Acetamidophenol (7,4 g; 49 mmole), finely powdered KOH (2,76; 49 mmole), 5% tetrabutylammonium bromide and a volume of tetrahydrofuran (THF) (30 ml) were added to a solution of a tosylether of PVAL (4,7 g; 16,4 mmole) in THF (50 ml). The reaction mixture was heated at 80°C for 6 h, with continued stirring.

The solvent was then removed under reduced pressure on a rotary evaporator and ice-cold water (100 ml) added to the residue. The product was filtered and washed with 6% NaOH (50 ml) and then with water to remove unreacted p-acetamidophenol.

% Substitution of the p-toluenesulphonylester (37,1% tosylated PVAL) by p-acetamidophenol, as determined by ^{1}H-NMR spectroscopy was 75,2% and the % yield was 67,5%.

Step 3: Hydrolysis of p-acetamidophenylether of PVAL to polyvinyl alcohol-co-vinyl p-aminophenylether

A solution of p-acetamidophenolester of PVAL (3 g) in ethanol (100 ml) and a volume of 12% ethanolic HCl (100 ml) were introduced into a glass tube. A vacuum was drawn and the glass tube sealed. Hydrolysis was carried out at 100°C for 24 h in this sealed container. Polyvinyl alcohol-co-vinyl p-aminophenylether was isolated by precipitation in acetone and washing. The product was dried on a vacuum pump for 6 h.

3.1.3.2 Preparation of the crosslinking agent

1,2 Benzenedicarbonyl dichloride is commercially available and was recrystallized from petroleum ether (bp. 60 - 80°C).

3.1.3.3 Fabrication and test results of tubular RO membranes of polyvinyl alcohol-co-vinyl p-aminophenylether

The membranes were prepared by depositing a thin layer of a dilute aqueous solution of the modified polyvinyl alcohol (PVACVAPE) on the surface of a polysulphone support membrane, which had been stored in water and then drained for 5 min, and subsequently contacting the polymeric precursor layer with either a dilute solution of an acid scavenger followed by a dilute hexane solution of the crosslinking agent or vice versa. Dilute aqueous solutions of NaOH or dilute hexane solutions of triethylamine (TEA) was used as the acid scavenger. Membranes were made by hand, in a tubular form (tube i.d. 13 mm, length 0.5 m), and dried at elevated temperature (93°C about 5 min). Details of the various fabrication processes used, are given in Tables 1 to 4. Typical RO performances results are included.

TABLE 1:

Membrane fabrication formulation used for making of PVACVAPE/IPC membranes and RO performance recorded - Method 1

Concentration of modified PVAL precursor	(% m/m)	0.5
Precursor contact time	(min)	5
Precursor draining time	(min)	2
Concentration of acid scavenger (NaOH)	(% m/m)	0.5
Acid scavenger contact time	(min)	0.5
Acid scavenger draining time	(min)	5
Concentration of crosslinking agent	(% m/m)	1
Crosslinking contact time	(min)	1
Post-crosslinking air drying time	(min)	5
Oven temperature	(°C)	93
Oven residence time	(min)	5
RO performance	Salt retention (%)	33.63 ± 1.86
(after 155 h)	Permeate flux (lmh)	33.91 ± 3.45

TABLE 2:

Membrane fabrication formulation used for making of PVACVAPE/IPC membranes and RO performance recorded - Method 2

Concentration of modified PVAL precursor	(% m/m)	0.5
Precursor contact time	(min)	5
Precursor draining time	(min)	5
Concentration of crosslinking agent	(% m/m)	1
Crosslinking contact time	(min)	1
Post-crosslinking draining time	(min)	2
Concentration of acid scavenger (TEA)	(% m/m)	0.5
Acid scavenger contact time	(min)	0,5
Acid scavenger air drying time	(min)	5
Oven temperature	(°C)	93
Oven residence time	(min)	5
RO performance (after 285 h)	Salt retention (%)	46,54 ± 2,18 41,03 ± 2,3
	Permeate flux (lmh)	17,23 ± 1,46 19.9 ± 1,99

TABLE 3:

Membrane fabrication formulation used for making of PVACVAPE/IPC membranes and RO performance recorded - Method 3

Concentration of modified PVAL precursor	(% m/m)	0,5
Precursor contact time	(min)	5
Precursor draining time	(min)	5
Concentration of acid scavenger (TEA)	(% m/m)	0,5
Acid scavenger contact time	(min)	0,5
Acid scavenger draining time	(min)	2
Concentration of crosslinking agent	(% m/m)	1
Crosslinking contact time	(min)	1
Post-crosslinking air drying time	(min)	5
Oven temperature	(°C)	93
Oven residence time	(min)	5
RO performance	Salt retention (%)	31.37 ± 1,24
(after 186 h)	Permeate flux (lmh)	31,92 ± 2,18

TABLE 4:

Membrane fabrication formulation used for making of PVACVAPE/IPC membranes and RO performance recorded - Method 4

Concentration of modified PVAL precursor	(% m/m)	0.25
Concentration of PVAL	(% m/m)	0.25
Precursor contact time	(min)	5
Precursor draining time	(min)	2
Concentration of acid scavenger (NaOH)	(% m/m)	0.95
Concentration of m-phenylenediamine	(% m/m)	0.5
Acid scavenger contact time	(min)	0.5
Acid scavenger draining time	(min)	5
Concentration of crosslinking agent	(% m/m)	1
Crosslinking contact time	(min)	1
Post-crosslinking air drying time	(min)	5
Oven temperature	(°C)	93
Oven residence time	(min)	5
RO performance (after 186 h)	Salt retention (%) Permeate flux (lmh)	53.29 ± 3.59 3.18 ± 0.21

3.1.3.4 Test Conditions

The membranes, made by the four different methods, were tested for their RO performances of salt retention and rate of water permeation in a closed-loop system. Conditions used for the testing are given in Table 5. Results given are the average of three membranes. Method 2 was repeated and two separate evaluations were made on the six membranes.

TABLE 5:

Conditions used for the testing of modified PVAL (PVACVAPE/IPC) membranes

Operating pressure	2.2 MPa
Feed-water temperature	20°C
Feed-solution composition (NaCl or $MgSO_4$ in distilled water)	2 000 mg/ℓ
Test time	> 155 h
pH	6.4 - 6.8
Linear Flow Velocity	600 ℓ/h

3.1.4 RESULTS AND DISCUSSION

Membranes made from polyvinyl alcohol-co-vinyl p-aminophenylether, using methods 1, 2 and 3, gave retentions of between 31,4 and 46,5% for 2 000 ppm NaCl feed solutions and fluxes ranged from 17,2 to 33,9 lmh.

Membranes which were made from an admixture of polyvinyl alcohol-co-vinyl p-aminophenylether, PVAL and m-phenylenediamine by method 4 gave an average retention of 53,29 + 3,59% and flux of 3,27 ± 0,14 lmh. Results of membranes fabricated by the different methods are shown graphically in Fig. 1.

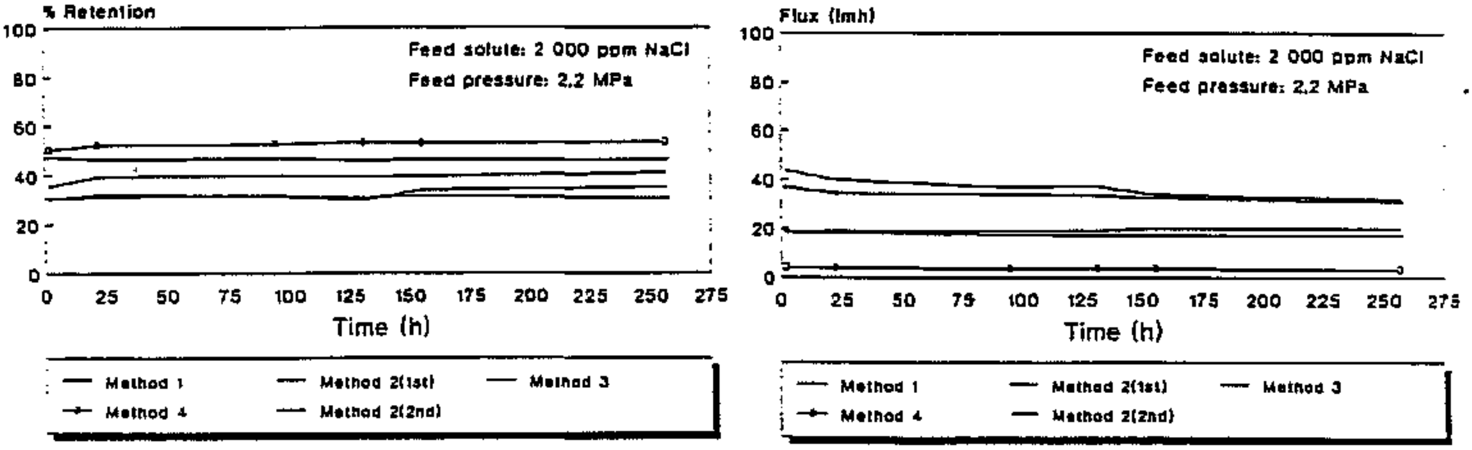

FIGURE 1:
A comparison of RO performances of membranes made from p-aminophenyl ethers of PVAL (PVACVAPE), by methods 1-4

Membranes made by methods 2 and 5 were tested with a 2 000 ppm $MgSO_4$ feed solution and retentions of between 89,48 ± 3,3 and 90,80 ± 3,12% were obtained.

A summary of the percentage salt retentions and fluxes of membranes prepared by the four different methods, and tested with two different feed solutions of 2 000 ppm NaCl or $MgSO_4$ at 2,2 MPa are summarized in Table 6.

TABLE 6:
Summary of percentage salt retentions and fluxes obtained for PVACVAPE/IPC membranes prepared by four different methods

(Membranes tested with feed solution of 2 000 ppm NaCl or $MgSO_4$, at pressure of 2,2 MPa)

Method	NaCl feed			$MgSO_4$ feed		
	Retention (%)	Flux (lmh)	Time (h)	Retention (%)	Flux (lmh)	Time (h)
1	33,63 ± 1.86	33,91 ± 3.45	154			
2 (I)	46,54 ± 2,19	17,23 ± 1.46	286			
2(II)	41,03 ± 2,31	19,81 ± 1,99	240	89.48 ± 3.33	18.88 ± 2.02	160
3	31.37 ± 1.24	31,92 ± 2,18	186			
4	53.29 ± 3.59	3,18 ± 0,21	212	90.80 ± 3.12	3.27 ± 0.14	193

Method 2 gave membranes with the best NaCl retentions, but the lowest flux. There was no significant difference between retentions and fluxes of membranes prepared according to methods 1 and 3. The fluxes of membranes prepared by method 1 were not stable over an extended period (there was a marked flux decline after 439 h), whereas the fluxes of membranes made by method 2 were much more stable over a long period. The stabilities of fluxes of membranes prepared by method 3 were also more stable than those prepared by method 1. These early results prompted the choice of method 2 as the process by which further membranes of polyvinyl alcohol-co-vinyl p-aminophenylether were to be made.

Addition of m-phenylenediamine to the precursor solution for making membranes by methods 4 led to improved the retention of the membranes, but also decreased the flux to a level which was unacceptable for RO membranes. During the manufacture of membranes by methods 4, two layers of precursor are formed, namely, the layer of polyvinyl alcohol-co-vinyl p-aminophenylether-polyvinyl alcohol and the m-phenylene diamine layer. A possible reason for the low fluxes of these membranes could be that the thin film formed during cross-linking was too thick, because of the presence of two layers which could react with the crosslinking agent, creating a thicker dense barrier and restricting the flow of water through the membrane.

3.1.5 CONCLUSIONS

1. The copolymer, polyvinylalcohol-co-vinyl p-aminophenylether (PVACVAPE) was synthesized by the chemical modification of PVAL, rather than copolymerization.

The synthetic pathway for the preparation of polyvinyl alcohol-co-vinyl p-aminophenylether included:

1) The synthesis of the p-toluenesulphonylester of PVAL from PVAL and p-toluenesulphonyl chloride;
2) The synthesis of the p-acetamidophenylether of PVAL from the p-toluenesulphonylester of PVAL and p-acetamidophenol;
3) Hydrolysis of the p-acetamidophenylether of PVAL to the polyvinyl alcohol-co-vinyl p-aminophenylether.

2. The fabrication of the RO composite membranes was carried out, using three steps. Three different methods of membrane fabrication were used and all membranes were evaluated. Method 2, which entailed the crosslinking of polyvinyl alcohol-co vinyl p-aminophenylether and IPC followed by treatment with an acid scavenger (TEA), gave membranes with the highest RO performances.

3. The percentage retention obtained with a 2 000 ppm NaCl solution at 2,2 MPa for membranes made by method 2 was 46,5 ± 2,18% after 240 h of testing, and the flux was 17,2 ± 1,46 lmh; these values were reasonably stable over this period of testing. These membranes gave retentions of 89,48 ± 3,33% for a 2 000 ppm $MgSO_4$ solution, after testing for 300 h.

4. Membranes fabricated from an admixture of m-phenylenediamine and polyvinyl alcohol-co vinyl p-aminophenylether gave the highest retentions for a 2 000 ppm NaCl solution, 53,29 ± 3,59%, but the fluxes were very low (3,18 ± 0,21 lmh) and were therefore not practically suitable as RO membranes.

3.2 POLYVINYLIMIDAZOLINE RO MEMBRANES

3.2.1 INTRODUCTION

The aim of this study was to investigate the use of polymeric precursor compounds with 2-imidazoline structure in the fabrication of UTF RO membranes. This followed from the premise that the water soluble, amine containing material, poly-2-vinylimidazoline (PVI) could be synthesized inexpensively and simply from available reagents [1]. A second reason for using such a chemical compound as a UTF membrane precursor was that the nitrogen atoms have only one reactive site and are not part of the main polymer chain [2]. Upon reaction of homopolymeric PVI with an acidic chloride crosslinking agent, tertiary amide groups sould be formed. Having any nitrogen-containing groups which might be susceptible to chlorination, causing subsequent deterioration of the membrane, in the polymer side chain, was thought to offer a possible way of increasing resistance of a membrane to degradation by chlorine [3].

It was, furthermore, desirable to use novel aromatic chemical crosslinking components which contained sulphonyl chloride groups and which varied in functionality. Incorporation of sulphonate groups in membrane structures could result in increases in retention, flux and fouling resistance of the membrane [4].

The chemical reactions which occur during the creation of the UTF RO membranes by interfacial polycondensatiuon reactions are only partially understood. The crosslinked interfacial film is often less than 300 nm thick and because there are indications that such a thin-film desalting barrier is not homogeneous but varies in both chemical structure and degree of crosslinking through its thickness, techniques must be found to shed more light on the membrane chemistry. Further objectives were to create some of the model structures expected to be formed in the ultrathin film and to study the chemical behaviour of the different functional groups under conditions similar to those under which membranes were used. This would, unfortunately, be limited to the study of reactions in solution and not in an ultrathin crosslinked film.

In the event of this study leading to the creation of efficient RO membranes, the novel chemical system was to be optimized in order to achieve formation of an ultrathin-film structure with high membrane performance [5].

3.2.1.1 Objectives

The objectives of this research were therefore:

- (i) to synthesize and characterize PVI and selected crosslinking agents;
- (ii) to study certain selected membrane fabrication conditions and the effect of variations on the resulting membrane performance;
- (iii) to ascertain what the effect of various operating conditions may have on a PVI UTF membrane, including testing the membranes with chlorinated feedwaters and with feed solutions of high and low pH;
- (iv) to study the chemistry of PVI and to obtain insight into the reactions which this compound undergoes with aromatic acid chloride crosslinking agents in the

fabricated of UTF RO membranes and into the chemical composition of a final PVI/SCI desalting barrier;

(v) to use PVI in a mixture with selected hydrophilic materials, as precursor in fabrication of modified membranes and to test these.

To meet the objectives of the research, a number of tasks was undertaken, as given below.

(a) Synthesis and characterization of PVI

As very little was known of PVI, various synthesis routes were to be studied and attempts made to characterize the products. If, after synthesis, more than one functional group was found to be present in the product, it would be necessary to study the effect of such chemical variations on the chemistry and performance of the ultrathin film.

(b) Synthesis and use of aromatic crosslinking agents containing sulphonyl chloride groups

The compounds to be synthesized were:

3-Chlorosulphonylbenzoyl chloride (SCI)
3,5-Dichlorosulphonylbenzoyl chloride (Cl2S)

Membranes were to be fabricated using an PVI precursor and the different crosslinking agents and then tested for their RO performance.

(c) Creation of novel PVI/SCI and PVI/Cl2S UTF membranes, using various fabrication conditions, and determination of their RO performances

The formation of any membrane system involves a multitude of fabrication variables, such as concentration of reagents, contact time and conditions of heat-curing, all of which are, furthermore, interrelated. A number of combinations of these variables was to be used in the fabrication of UTF RO membranes from PVI as polymeric precursor and a sulphonate-group-containing compound as the crosslinking agent. The objectives of this operation were to:

(a) obtain indications as to the salt retention and water permeability capability of the PVI UTF RO membranes;

(b) attempt to determine, by changing one variable at a time, which fabrication variables appeared to have the most significant effects on RO membrane performance;

(c) arrive, by this approach, at a set or sets of fabrication conditions under which flat-sheet PVI UTF RO membranes of high baseline RO performance could be fabricated.

(Information obtained during this phase of the research was used later as the basis for the choice of levels for fabrication conditions during the development of a method for the mathematical optimization of PVI/SCI membranes in tubular form, during a parallel project [5].)

(d) Evaluation of the stability of PVI/SCI membranes at low and high pH, and in a chlorine environment

PVI/SCl membranes were to be prepared and evaluated for their RO performance after they had been exposed to harsh operating conditions imposed by feedwaters containing chlorine and by feedwaters if high and low pH.

(e) Preparation of the monomeric model compounds representing the functional groups hypothesized to be present in the PVI/SCl membrane and study of their reactions in low and high pH media and in a chlorine environment

Model-compound studies were carried out on the monomeric forms of the repeat units of the effective PVI/SCl UTF RO membrane. To this end, model compounds were selected, synthesized and characterized. They were then exposed to chlorine-containing solutions and solutions of high and low pH, and their stability or reactivity under such conditions determined.

The aim of this study was basically to investigate the usefulness of the results obtained from the model compound studies in explaining any change in membrane performance which occurred, at the molecular level, after exposure of the membranes to chlorine-containing feedwater and to low and high pH media.

3.2.2 LITERATURE SURVEY

A historical and theoretical background, concerning the topics: reverse osmosis-membranes and applications, UTF composite membranes - their preparation, chemical compositions, RO performances (including stabilities in chlorinated waters and waters of low and high pH), polyamides and poly-2-vinylimidazoline has been presented as part of a Ph.D.-thesis, "The Chemistry of Poly-2-vinylimidazoline Reverse Osmosis Membranes", by M.J. Hurndall [6].

3.2.3 MATERIALS AND METHODS

Experimental condition, pertaining to: the synthesis of PVI precursor materials, crosslinking agents and model compound materials; the fabrication and testing of membranes and the characterization of PVI by ^{13}C nmr spectroscopy have all been described in detail in Chapter 3: Equipment and Experimental Methods of Ref. [6]

3.2.4 RESULTS AND DISCUSSION

Detailed results of the work and the relevant discussions have been presented in Addendum 4, Chapter 4. Highlights of the achievements of this study only, and conclusions are given here.

1. Poly-2-vinylimidazoline (PVI) can be used as precursor material in interfacial reactions to make efficient RO membranes. These could be made in both flat-sheet and tubular forms. Two different polymer products, termed PVI-OD and PVI-FD, were obtained by using two different sets of reaction conditions. PVI was characterized by ^{13}C nmr spectroscopy and found to be a copolymer, comprising ring-closed (imidazoline) and its hydrolyzed form and ring-opened (amide) repeat units. PVI-CFD was obtained after partial purification of PVI-FD.

   The use of PVI, with its nitrogen atoms being pendent to the hydrocarbon chain, resulted in some increase in chlorine-tolerance of the membranes. This chlorine-tolerance was greater than that of membranes made with the aliphatic polymeric precursor PEI (NS-100/1 membranes) [7], but not as great as that of membranes made from the aromatic precursor phenylenediamine (FT-30 membranes) [8, 9].

2. The use of aromatic crosslinking-agents containing sulphonyl chloride groups; in addition to carboxylic acid chloride groups, illustrated the importance of the chemical nature of the reactive groups and of the effect which the structure of the reactants has on membrane structure, as reflected in the RO performance of the membranes. In terms of membrane performance, the use of the crosslinking agents 3-chlorosulphonylbenzoyl chloride (SCl) and 3,5-dichlorosulphonylbenzoyl chloride (Cl2S) gave flat-sheet membrane RO performances better than those of membranes prepared with the more generally used reagent, isophthaloyl chloride (IPC). For example:

    (a) Use of SCl instead of IPC gave PEI UTF membranes which gave higher flux and retention, as illustrated by the following RO performances:

    PEI/IPC membranes : 98,4% retention; 600 lmd flux
    PEI/SCl membranes : 98,7% retention; 835 lmd flux

    (Membranes were tested with 5 000 ppm NaCl solution at 4 MPa)

    (b) Use of SCl instead of IPC gave early PVI UTF membranes which gave higher retention, as illustrated by the following RO performances by flat-sheet membranes:

    PVI/IPC membranes : 72,7% retention; 1 760 lmd flux
    PVI/SCl membranes : 84,6% retention; 680 lmd flux

    (Membranes were tested with a 5 000 ppm NaCl solution at 4 MPa)

    (c) Use of the trifunctional reagent Cl2S gave PVI UTF membranes which gave higher retention and flux than those of membranes prepared with SCl, as illustreated by the following results:

    PVI/SCl membranes : 84,6% retention; 680 lmd flux
    PVI/Cl2S membranes : 96,4% retention; 800 lmd flux

    (Membranes were tested with a 5 000 ppm NaCl solution at 4 MPa)

3. Numerous fabrication variables were found to be important in the preparation of efficient PVI UTF membranes; slight variations led, in some cases, to large variations in membrane performance. Of the variables studied, those considered most important were: polysulphone (PS) substrate, chemistry of the crosslinking agent, concentration of crosslinking agent and of precursor, addition of acid acceptor to the precursor solution and heat-cure temperature.

    The best RO performance results obtained for PVI-OD/SCl membranes in flat-sheet form were:

94,3 ± 1,2% retention; 1 096 ± 50 lmd
(tested for 5 000 ppm NaCl at 4 MPa)

97,4 ± 1,4% retention; 400 ± 22 lmd
(tested for 2 000 ppm NaCl at 2 MPa)

The optimum RO performances of PVI-OD/SCI tubular membranes (developed during a parallel study) were:

97,1 ± 0,1% retention; 730 ± 24,1 lmd
(tested for 2 000 ppm NaCl at 2 MPa)

The optimum RO performances of PVI-FD/SCI tubular membranes (developed during a parallel study) were:

98,2 ± 0,7% retention; 560 ± 150 lmd
(tested for 2 000 ppm NaCl at 2 MPa)

Initial results of "unoptimized" RO performances of PVI-CFD/SCI tubular membranes were:

97,0 ± 1,1% retention; 643 ± 74 lmd
(tested for 2 000 ppm NaCl at 2 MPa)

4. Exposure of PVI UTF membranes to chlorine is not advisable. It is, however, proposed that exposure of PVI-FD/SCI membranes to 5 ppm chlorine at pH 6 to 7 for a short period of time would be tolerated. Prolonged exposure to chlorine results in irreversible decline in retention.

   Maximum performance of PVI-FD/SCI tubular membranes has been recorded in the pH 6,5 to 7 range. These membranes can be safely used over a pH range of 4,5 to 8,5.

   Exposure of membranes to solutions of pH 3 over a period of one month under dynamic conditions, led to a drop in baseline retention performance and increase in flux. Under similar conditions at pH 11, the membranes showed only a slight drop in retention but an almost doubling in flux.

   After static storage of membranes at pH 3 there was a rapid and irreversible decline in membrane performance. Similar storage of membranes at pH 11 caused no decrease in salt retention but an almost doubling influx.

   Flat-sheet PVI/SCI membranes may be operated at temperatures of up to 40°C. Compared with the performance of membranes operated at 25°C, the salt retention by membranes operated at 40°C was unaffected, but fluxes were almost doubled.

5. The use of model compounds to study the effect of external variables on groupings typical of those found in a PVI/SCI ultrathin films revealed the problems associated with hydrolytic stability which could arise in the UTF membrane: during synthesis of the PVI precursor, during formation of the PVI UTF membrane and during operation of the membrane. Model compound studied proved to be very valuable in characterizing batches of PVI by ^{13}C nmr

spectroscopy. However, the results of the studies of the reactions of the PVI/SCl membranes model compounds could not adequately explain changes, at the molecular level, in the membrane performance under harsh operating conditions. It is nonetheless suggested that model compound studies should be carried out in parallel with chemical studies on any future novel UTF membrane system development.

6. By incorporation of various hydrophilic additives into a PVI-precursor solution, piperazine, PVAL or HA-1, UTF membranes were obtained which were considered adequate for low-pressure applications (< 200 kPa).

PVI FD-PVAL/SCl membranes and PVI-FD + HA-1/SCl membranes exhibited stable performance over an extended test period of 200 h which exceeded the performance of a PVI-FD/SCl control membrane: 90% retention and 200 lmd flux at 500 kPa applied pressure was achieved. A selected of these membranes were used for tests on industrial wastewater (see section 4 and 2.5.5).

Several publications have resulted from the work carried out on PVI membranes, including:

(a) New composite reverse osmosis membranes made from poly-2-vinylimidazoline;
(b) The performance of novel reverse osmosis membranes made from poly-2-vinylimidazoline;
(c) Chemical composition of thin-film composite reverse osmosis membranes made from poly-2-vinylimidazoline;
(d) Modified poly-2-vinylimidazoline reverse osmosis membranes;

A further two publications have recently been submitted for consideration for publication:

(e) Characterization of copolymeric poly-2-vinylimidazoline (to J. Applied. Polymer Science);
(f) Optimization of the fabrication variables of poly-2-vinylimidazoline tubular RO membranes (to Separation Science and Technology).

Copies of these have been included in Addendum 1.

3.2.5 CONCLUSIONS

Research into the making of UTF membranes from PVI precursors is considered complete, unless we are requested to carry out specific further investigations, e.g. recommended post-fabrication storage conditions. PVI/SCl membranes can offer performances of typically 97,8% retention and 600 lmd flux (for 2000 ppm NaCl at 2 MPa). Latest results have indicated, however, that modified PVI membranes (membranes made from admixtures of PVI and piperazine or PVAL) might be suitable for low pressure application. Typical results of 90% retention and 200 lmd flux at 500 kPa have been achieved.

At the request of industry, attempts were made to upscale these membranes and modularize them for testing on genuine industrial effluent. A description of such membranes and their test results have been presented in detail in section 4.

3.2.6 REFERENCES

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4. MODULARIZATION OF RO MEMBRANES

4.1 INTRODUCTION

The Institute was approached by Membratek to produce PVAL membranes, then still under development, for field trials by DEBEX. The objective was to desalinate brackish water to a potable standard, in compliance with SABS specifications. The feedwater contained $CaSO_4$ and NaCl at a TDS content of approximately 3 000 mg/l. The water was at a temperature of 38°C and contained no free chlorine. The membranes were required to have a high salt retention (>90% NaCl) at relatively low pressures (2 - 3 MPa).

This section describes the manufacturing conditions used in the preparation of the membranes made for this application, and the problems encountered in the modularization of the membranes.

Research conducted into these membranes was as described in sections 2.4.3 and 3.2.

4.2 SUPPORT MEMBRANES.

Membratek supplied 13 mm M719 and M719L tubular membranes for coating with the appropriate polymer film.

4.3 MEMBRANE TYPES.

The following UTF reverse osmosis membranes were selected for manufacture and evaluation. All the membranes, with the exception of those designated CAMOH 5, were made using the M719L supports.

a) PPIP membranes

b) CAMOH 5 membranes

c) CAMPIP 3 membranes

PPIP membranes were made from a precursor of PVAL + PIP; CAMOH 5 membranes were made from a mixture of PVAL + PVI, and CAMPIP membranes were made from a mixture of PVI + PIP.

These membranes were all manufactured by:

1) pre-draining of the support membrane;

2) dipping the support membrane into an aqueous precursor solution;

3) draining to remove excess solution;

4) dipping into a solution of a multifunctional acid chloride (IPC or SCl) in hexane;

5) air drying to remove excess solvent; and

6) heating the resultant membrane in an oven to complete the crosslinking reaction.

4.3.1 PPIP MEMBRANES

The fabrication and evaluation of the different types of PPIP membranes were described in section 2.4.3.3a.

4.3.2 CAMOH 5 MEMBRANES

These were based on modified PVI flat-sheet membranes (see Addendum 4, section 4.4.4.3).

Components of the solutions used in membrane fabrication are given in Table 7.

<u>TABLE 7</u>:
Aqueous and organic phases for the fabrication of CAMOH 5 membranes

AQUEOUS PHASE		ORGANIC PHASE	
COMPONENT	QUANTITY (mass%)	COMPONENT	QUANTITY (mass%)
PVI FD	0,96	SCl	3.00
PVAL	0.24	Hexane	97.00
TEA	0.20		
TSP	0,50		
H_2O	98.10		

The manufacturing conditions for CAMOH 5 membranes were as follows:

TABLE 8:

Basic conditions adhered to in the production of CAMOH 5 membranes

PARAMETER	VALUE
Pre-drain:	10 min
Aqueous dip:	15 min
Post drain:	8 min
Organic dip:	5 min
Air dry:	16 min
Oven temperature:	95 °C
Curing time:	5 min

4.3.3 CAMPIP 3 MEMBRANES

CAMPIP 3 membranes were prepared as described in Addendum 4, section 4.4.4.3.

TABLE 9:

Aqueous and organic phases for the fabrication of CAMPIP 3 membranes

AQUEOUS PHASE		ORGANIC PHASE	
COMPONENT	QUANTITY (mass%)	COMPONENT	QUANTITY (mass%)
PVI FD	1,08	SCl	3.00
PIP	0,12	Hexane	97.00
TEA	0,20		
TSP	0,50		
H_2O	98,10		

The fabrication conditions for the CAMPIP 3 membranes are identical to those used in the production of CAMOH 5 membranes.

4.4 RESULTS

4.4.1 TEST 1

Two membranes (diameter = 13mm, length = 400mm) of each of the three types mentioned above were produced for initial evaluation.

From the performance of the PPIP membranes (section 2.4.3.3) it was clear that the membrane designated M1X1 was the best PPIP membrane for this particular application. All the CAMOH 5 and CAMPIP 3 membranes gave results better than values specified by MEMBRATEK. The results are shown in Figures 2 and 3.

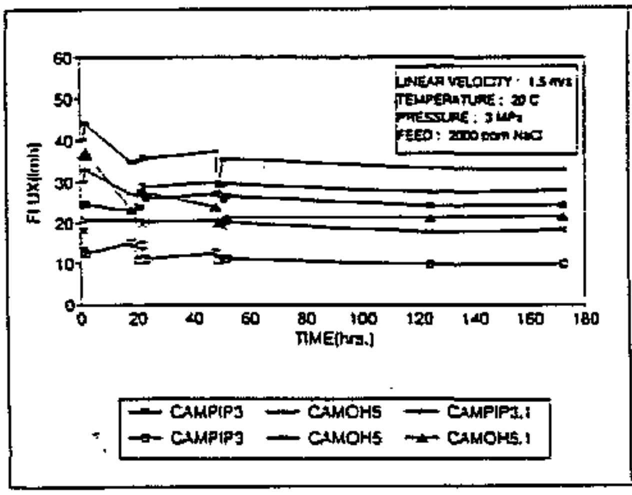

Figure 2:
CAMOH and CAMPIP membrane flux vs. time

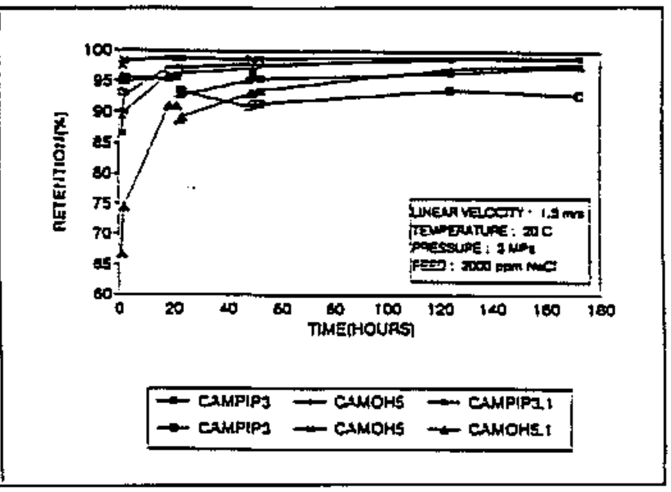

Figure 3:
CAMOH and CAMPIP membrane retention vs time

4.4.2 TEST 2

When the test results obtained from the modules (see 4.4.3) were found to compare unfavourably with those obtained in Test 1, the same membranes used in Test 1 were re-evaluated on the single cell rig. It is important to note that the membranes had dried out in the interval, due to pump failure, between tests 1 and 2.

The results obtained on this second evaluation are compared with those of other tests in Figures 4 and 5.

4.4.3 TEST 3

The three membrane types showing the best results (PPIP M1X1, CAMOH 5, and CAMPIP 3) were chosen for the production of modules. The following modules were assembled by MEMBRATEK from membranes produced at the IPS.

TABLE 10:
Modules assembled by MEMBRATEK

CODE	SUPPORT	DESCRIPTION	*MODULES
M1X1	M719L	PVAL + PIP + IPC	2
CAMPIP 3	M719L	PVI + PIP + SCI	3
CAMOH 5	M719L	PVI + PVAL + SCI	2
CAMOH 5N	M719	PVI + PVAL + SCI	1

*Each 1.2-metre module contained nineteen 13mm tubes.

The module results are compared to the single cell results in Figures 4 and 5.

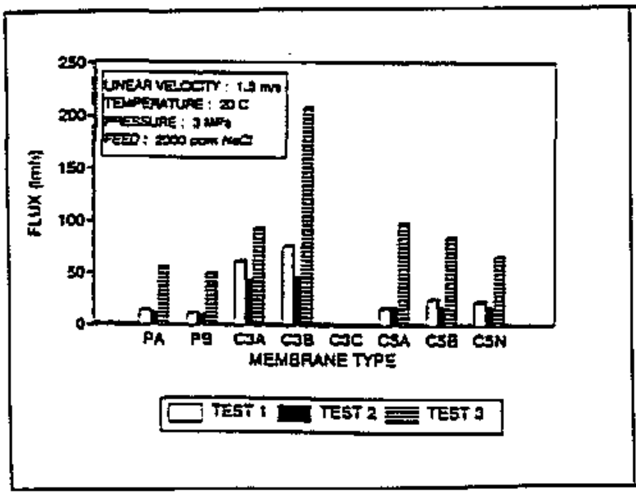

Figure 4:
Comparison of fluxes obtained in tests 1, 2, and 3

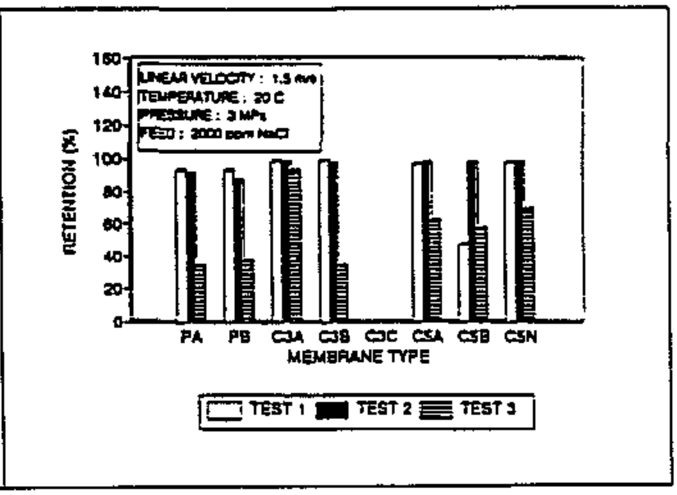

Figure 5:
Comparison of retentions obtained in tests 1, 2, and 3

PA : PPIP A	PB : PPIP B
C3A : CAMPIP 3A	C5A : CAMOH 5A
C3B : CAMPIP 3B	C5B : CAMOH 5B
C3C : CAMPIP 3C	C5N : CAMOH 5N

4.4.4 TEST 4

After finding that the RO performance of modules was below that of the single membranes tested prior to modularization, permission was obtained to open one of the modules (CAMPIP 3B). Each membrane was cut into two 400mm sections for evaluation on the single-cell rig. The results are contained in Figures 6, 7, and 8.

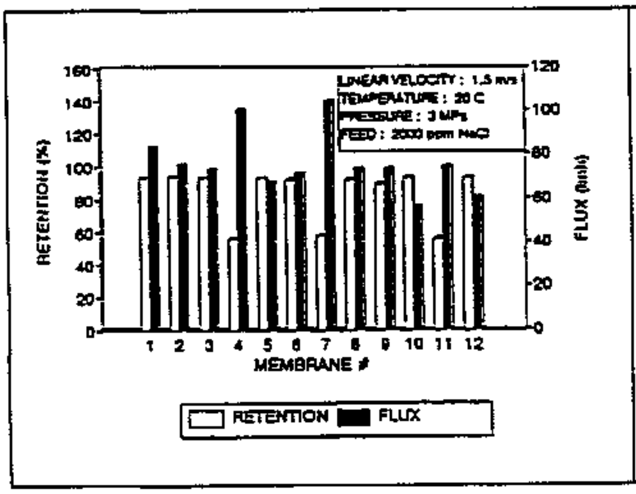

Figure 6:
Reopened CAMPIP module results. Tubes: 1 to 12

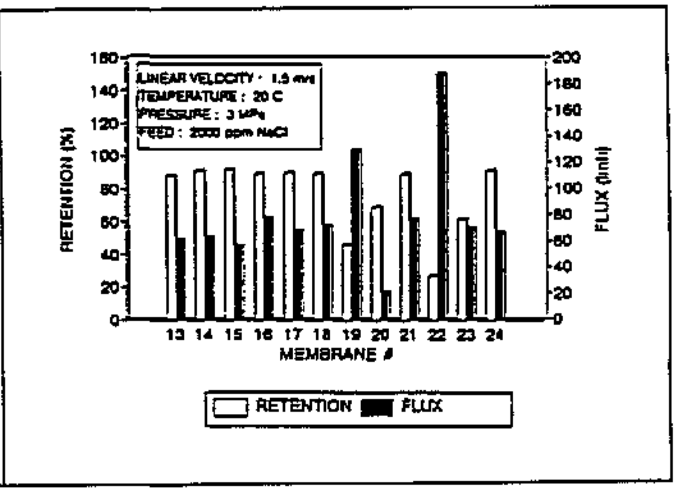

Figure 7:
Reopened CAMPIP module results. Tubes: 13 to 24

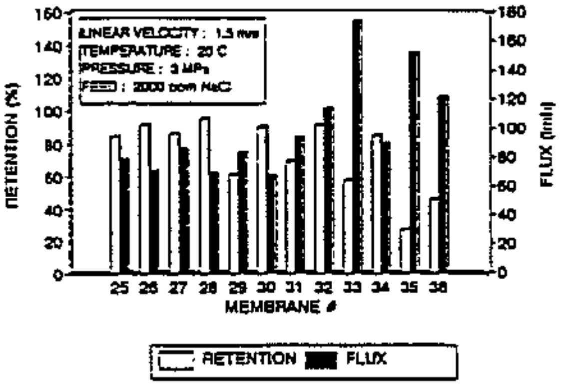

FIGURE 8:
Reopened CAMPIP module results. Tubes: 25 to 36

4.5 DISCUSSION

From the data in Figures 4 and 5 it was clear that the membranes were up to specification when tested as single tubes. Little or no deterioration was evident, even after the membranes were stored for 30 days prior to Test 2. Most of the membranes recovered from the CAMPIP 3B module still gave retentions of approximately 90%; only a few of the sections tested gave low retentions (Figures 6, 7, and 8). The average retention for the recovered membranes was 78,8% (flux = 85,4 lmh) compared with 34% (flux = 208 lmh) for the module. From these findings it was evident that the poor performance of this module was due to failure of only a few of the membrane units in the module. One module (CAMPIP 3B) showed no flux at all (even at a pressure of 4MPa). This could have been due to very tight membranes or problems with the membrane module.

It is highly recommended that investigations be carried out to ascertain the cause of the failure of the membrane module.