EXECUTIVE SUMMARY

INDUSTRIAL APPLICATIONS OF MEMBRANES

Final Report to the

Water Research Commission

by

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WRC Project No 362/1/95
ISBN 1 86845 194 1

April 1995

1. INTRODUCTION

Membrane separation technology resulted from a single event; the development of the synthetic asymmetric membrane in 1960 at the University of California, Los Angeles, by Sourirajan and Loeb. Since then it has spawned a vast array of diverse applications, almost unmatched by any other separation process. Desalination and water treatment by reverse osmosis (RO) are probably the earliest and best known of these applications.

RO is essentially a dewatering process, whereas ultrafiltration (UF) is a fractionation technique that can simultaneously concentrate macromolecules or colloidal substances in process streams. Nanofiltration (NF) falls between these two processes.

General advantages of the use of membrane systems for separations include:

i. the relatively simple design of membrane systems;

ii. the modular nature of membranes make expansion of the system easy;

iii. the adaptability of membrane systems to changing feed streams;

iv. often less energy is required, compared to the requirements of conventional treatment systems; and

v. membrane systems have potentially lower capital and operating costs than conventional treatment systems.

The objectives encompass the laboratory evaluation of various experimental membranes made at the Institute for Polymer Science (IPS) and made available in development quantities for use on real or simulated effluents, including evaluation at industrial sites. Interactive participation would form a large part of the work.

Membrane performance restoration was also to receive attention. Suitable cleaning regimes were required to solve the problem of permanent flux decline, for example in membranes operated on abattoir effluent streams and for capillary membranes used in the pretreatment of seawater for RO desalination. Membrane performance restoration was also to be approached by re-investigating the technique of supplemental polymer coatings (prompted by a request from Eskom, for the regeneration of their substandard cellulose acetate (CA) membranes at the Koeberg RO plant). Regeneration chemistry was to be studied and an acceptable regeneration formulation and procedure established for CA membranes.

2. OBJECTIVES

A broad approach was to be followed to meet the objectives of the contract. Broadly stated, the objectives were:

i. the on-site testing of established ultrafiltration (UF), reverse osmosis (RO) and nanofiltration (NF) membranes in various industrial applications;

ii. evaluation of experimental membranes to determine any possible shortcomings;

iii. the installation and evaluation of new membranes which became available through research on industrial effluents;

iv. address problems associated with membrane applications and operation, for example, cleaning of fouled membranes and membrane performance;

v. address problems in existing membrane systems by using experimental membranes with different physical properties, and the investigation of the use of various pretreatment methods;

vi. the design, construction and installation of test equipment for the above applications, as necessary; and

vii. studying the regeneration chemistry for CA membranes to establish an acceptable regeneration procedure.

2.1 ULTRA THIN FILM (UTF) RO MEMBRANES FOR BRACKWATER TREATMENT

IPS was requested to supply a selection of developmental and experimental RO membranes to be tested on-site in Botswana. The goal of the operation was to desalinate brackish water to a potable standard, complying with SABS specifications. The IPS was to provide Membratek with experimental UTF RO membranes which were to be potted into 1,2m modules before on-site installation. A selection of membranes was first to be manufactured on a laboratory scale and tested; then adequate membranes were to be manufactured on a larger scale. Batch tests were to be performed prior to sending the membranes to Membratek for potting into modules.

2.2 SASOL COOLING WATER BLOWDOWN

In industry, in a closed recirculating water system, an increase in salt and organic concentrations is inevitable. Scaling occurs in equipment and valves because of the salt build-up, while fouling results from the presence of organic substances and suspended solids in the effluent. One way of solving these problems could be by bleeding a constant stream of effluent to evaporation ponds. This is, however, not an ideal solution because of the high costs involved and the limited space available for building evaporation dams.

When problems arise in treating an industrial effluent, the following questions must be asked:

i. is an alternative method of treatment possible;

ii. where in the system does the highest salt and organic concentration occur; and

iii. which method would be the most suitable for solving the specific problem?

The improvement in the quality of effluent within the system would result in a decrease in external water intake. The salt and organic concentrations in wastewater could thereby be increased. This would result in a more effective discharge of water to evaporation ponds.

IPS ultrafiltration and reverse osmosis membranes were to be tested on Sasol effluent. Cooling water blowdown (CWBD) was selected as the most suitable stream with which to test the membranes because this effluent contained a variety of dissolved and suspended solids, both organic and inorganic. The idea was to remove most of the suspended solids and macromolecular substances in the effluent by ultrafiltration, while reverse osmosis would be applied for salt removal.

Established membranes, as well as experimental ones, were tested first on a laboratory scale at the IPS laboratories on Sasol CWBD. Because the effluent underwent chemical changes when stored for a period of time, it was of great importance to constantly work with a fresh effluent, in order to simulate true operating conditions during testing. After extensive in-house testing it was decided to rather test the membranes on-site at Secunda to achieve more reliable results. Three test-rigs were designed and constructed for installation. Tubular UF membranes, capillary UF membranes, NF membranes and various RO membranes were then tested on-site on CWBD. This investigation supplied valuable information regarding the performance of IPS membranes and also facilitated the identification of problems which arose, and which required specific solutions.

2.3 POTASSIUM BITARTRATE REMOVAL FROM WINE RESTS

The main objective of this study was to determine whether membrane processes could be applied to the fractionation of wine lees to produce usable by-products such as yeast cells, cream of tartar and proteins and in such a way contribute to a substantial reduction in the volume of effluent generated by the current techniques used. A most important by-product of wine lees is potassium bitartrate (KHT); which is expensive to import. The colloids and macromolecules in the wine lees could be separated by UF, while RO could be used to concentrate KHT, which passes through the UF membranes, and to purify the effluent for re-use as process water in the factory.

In this study, UF membranes were to be used to "wash" the wine lees slurry at different solids concentrations. The KHT-rich permeate collected from UF was then to be concentrated, using RO and NF, to allow subsequent precipitation of the product.

A NF pilot plant was installed at a local processing factory and valuable results regarding experimental NF membranes were obtained.

2.4 RESTORATION OF MEMBRANE PERFORMANCE

2.4.1 Cleaning of Polyethersulphone (PES) Tubular UF Membranes - Abattoir Case Study

The waste stream generated by a red meat abattoir represents both a serious potential pollution problem, since COD levels and phosphate levels are high, and a potentially valuable source of bio-material. Membrane filtration offers a possible solution to the treatment of abattoir process and rinse-water effluent. The objective of this study was to determine to what extent chemicals, known to the abattoir industry and used by them for sanitizing purposes, would be effective in restoring membrane productivity and to determine if and to what extent these chemicals might be harmful to the integrity of the membranes themselves.

2.4.2 UF in Seawater Pretreatment

The use of membrane filtration, in particular UF, to pretreat seawater which was to be desalinated by RO, was found to be competitive with other filtration processes. Low-cost Membratek tubular SWUF modules and IPS capillary UF modules were considered suitable for this application.

Mechanical and chemical cleaning regimes for the restoration of the fluxes of fouled membranes were to be investigated.

2.4.3 Supplemental Polymer Membrane Regeneration

The membrane regeneration project was re-initiated after Eskom's request for an investigation into the possibility of regenerating membranes in the RO plant at Koeberg. These spiral wound cellulose acetate (CA) membranes had been purchased from America and had been in operation for five years. The performance of these membranes had deteriorated to such an extent that they had become unfit for use. The membranes therefore either had to be replaced, or regenerated. The task set was to study regeneration chemistry in order to obtain a suitable regeneration procedure for these membranes.

The goal of the investigation was to develop a suitable coating formulation which would increase the retention of the membranes, without too great a loss in the rate of water permeation.

3. RESULTS AND CONCLUSIONS

3.1 UTF RO Membranes for Brackwater Treatment

For the purpose of desalinating brackish water to give a potable water which would comply with certain standards, tubular UTF RO membranes were manufactured for on-site testing in Botswana. The standards with which the membranes were to comply were: NaCl retention >90% at relatively low pressures of between 2 and 3MPa. The membranes were to be potted in modules, by Membratek, prior to installation on-site in Botswana.

Two experimental UTF RO membranes, produced at IPS, were selected for this purpose. They had been made and tested during a parallel Water Research Commission (WRC) project no 361, 1991-1993. The membranes were re-made in tubular form, on a laboratory-scale and the best-performing membranes selected for fabrication in greater quantities.

After potting of single tubes into modules, the membrane test results did not meet the required standards of performance. Later tests performed on single control membranes and membranes taken from the modules suggested that the membranes might have been damaged during module fabrication.

Further research is required to establish most favourable conditions under which to store these membranes, and to minimize damage during the assembly of the modules. This is currently being carried out as part of the Tolerant Membrane Project at IPS (1994-1996).

A UTF RO membrane comprises a thin and relatively brittle membrane layer upon a UF substrate membrane. For this reason it is important to handle these membranes with care during the potting process. The slightest hairline crack in the brittle ultra-thin layer could cause membrane performance to deteriorate.

The tubular membranes manufactured for the Botswana application were, however, successfully used in other applications (e.g. Sasol), where they were encased in perforated stainless steel tubes.

3.2 Sasol Cooling Water Blowdown

The quality of the process cooling water at Sasol has deteriorated over recent years. More specifically, the levels of sodium, chlorides, sulphates, chemical oxygen demand, and total suspended solids have increased by between 50 and 150% over the past five years.

Experimental UF and RO membranes were tested on Sasol CWBD. Different industrial effluents have different chemical compositions and therefore exhibit different properties. In the case of this particular effluent, the challenge to recover water to the extent that the water meets the desired standard for re-use, was hampered by the fact that the effluent contained a number of hydrophobic constituents which caused gel polarization at the membranes' surfaces. Permanent fouling could fortunately be prevented by means of regular detergent washes.

Ultrafiltration reduces the fouling potential of the effluent by the removal of suspended solids and macromolecules. It could therefore be used as a possible means of pretreating the effluent prior to RO or other desalting methods.

CWBD was regularly sent to Stellenbosch in 200ℓ drums. Various membranes were tested on this effluent. After extensive testing of tubular UF, capillary UF and NF membranes in the laboratory, the conclusion was reached that test-rigs should be designed and constructed to evaluate these membranes on-site, on a continuous stream of CWBD.

The UF and RO membranes evaluated during the course of this study proved to be, with the exception of a few, chemically stable after being tested on an effluent which consisted of a variety of dissolved and suspended solids and with a major fouling potential. It was also found that subjecting the UF membranes to a detergent wash always resulted in restoration of the original fluxes. It was found that suspended solids and macromolecules could be removed effectively by UF, while the salt concentrations were greatly reduced by RO.

A good quality permeate with 100% removal of suspended solids and close to 100% removal of colour was achieved by treating the CWBD with UF. This could result in a drastic increase in RO flux when UF is used as pretreatment method before RO. A cost study is required to determine whether this operation is economically viable in view of the rapid declining UF flux and the need for frequent washing to maintain high average flux-values. It was interesting to note that 50 to 70% of Fe^{3+} and SO_4^{2-} were removed because of the presence of a gel-layer on the UF membrane surface.

In the case of NF, the biggest problem proved to be the relatively rapid, although not permanent, fouling of the membranes. A general conductivity retention of approximately 70%, with 99% removal of PO_4^{3-}, SO_4^{2-} and colour were achieved with NF.

RO showed 95 to 99% conductivity retention, while individual retentions of Na^+, colour, F^-, PO_4^{3-}, K^+, SO_4^{2-} and Cl^- were never lower than 90%. Rapid fouling was again experienced, although the fouling was not permanent. Frequent detergent washes required during operation would probably make direct application of RO the least attractive operation.

In conclusion, it must be accepted that the effluent stream selected for testing of the membranes, namely CWBD, was an extreme case, especially as regards the fouling potential. It is almost certain that membrane performance, especially membrane flux, will improve when an alternate stream is selected. Evaluating membranes on site supplied valuable information regarding experimental membrane performance.

3.3 Potassium Bitartrate Removal from Wine Rests

The objective of this study was to determine whether membrane processes could be applied to the fractionation of wine lees to produce usable by-products such as yeast cells and cream of tartar (potassium bitartrate, KHT).

UF membranes were operated in diafiltration mode in order to "wash" the wine lees slurry at different solids concentrations. The KHT-rich permeate collected after UF was then concentrated using the processes of RO and NF to enable precipitation of the product (KHT).

Tests were conducted with experimental and commercial UF membranes at different solids concentrations. The wine lees slurry was alternately concentrated and then diluted with clean water until most of the KHT present in the feed was removed. UF membrane test results showed that while fluxes stabilized at a relatively high level of 50ℓmh, no permanent fouling occurred during tests. The permeate was collected for testing on RO and NF membranes.

Tests were conducted on the UF permeate with a commercial RO membrane and two different types of NF membranes. An experimental CA NF membrane gave good fluxes (double those of RO membranes) with KHT retentions of above 80%.

A NF membrane test unit was designed for installation at the factory at Brennochem. Experimental NF membranes were cast in a 1m module and installed at the factory. The membranes are still to be tested on "crystal water". This is an existing KHT-rich stream at the factory which compares well with the permeate of UF membranes operated on a wine lees slurry.

3.4 Cleaning Regimes

3.4.1 Cleaning of PES Tubular UF Membranes - An Abattoir Case Study

The short laboratory study conducted on membranes that had been obtained from the abattoir operating plant at Cato Ridge Abattoir revealed, amongst other things, the following:

i. there were indications that lipids were present on the surface of the membranes;

ii. low-temperature rinsing with cleaning solutions was not as effective as medium-temperature rinsing;

iii. proteolytic enzyme cleaners, especially those which have been developed and designed for use in the abattoir industry, were indeed effective in breaking up the foulant deposits;

iv. sponge balls were very effective in removing the loosened protein deposits by a scouring action, particularly if air was introduced to increase turbulence;

v. peptizing agents, such as chlor-alkalis, were effective in bringing about an improvement in membrane pure-water flux performance; and

vi. it was beneficial to membrane flux restoration if a proteolytic enzyme-cleaner rinse was followed by a chlor-alkali rinse.

3.4.2 UF Membrane Systems in Seawater Pretreatment by RO Desalination

Medium and low cut-off UF membranes used in the pretreatment of seawater for RO systems were found to be prone to fouling which resulted in a lowering of productivity. Tubular SWUF modules (13mm tube diameter) could be cleaned mechanically with sponge balls while in operation to maintain higher average flux values. In contrast, the tubular MEMTUF (9mm tube diameter) and capillary modules, which could not be cleaned by sponge balls, showed substantially lower, but stable, flux. The foulant could be removed by adopting a biochemical cleaning with a proteolytic enzyme, followed by a chlor-alkali rinse.

Further improvements in membrane performance will require further study of the membrane and plant operating parameters, in combination with cost-effective cleaning regimes for the different geometries.

On the basis of module material cost, the capillary format proved to be competitive with the SWUF technology, the lower flux being balanced by the reduced manufacturing cost.

3.4.3 Supplemental Polymer Coatings

Eskom's spent and below standard CA spiral wound modules were used for regeneration studies. Three methods of regeneration were investigated:

i. treatment of membranes with a resorcinol-formaldehyde resin;

ii. treatment of membranes with tannic acid and polyvinylmethylether; and

iii. treatment of membranes with poly(acrylic acid) and polyethylene glycol.

Regeneration of CA membranes was achieved by the treatment of membranes with coating materials to upgrade the performance of deteriorated or substandard membranes.

3.4.3.1 Resorcinol-formaldehyde Coatings

Both methods of circulation coating and dip-coating of membranes were effective in regenerating the CA RO membranes to some extent. Retentions of some membranes improved from as low as 65% to beyond 90%.

Higher molecular mass resins were more effective in regenerating membranes with retentions ranging from 60% to 80%, whereas lower molecular mass resins were more effective for membranes having retentions between 80% and 90%. Decreases were observed in the fluxes through the membranes (these were, however, also dependant on the state of deterioration of the membranes). Various combinations of formaldehyde/resorcinol coatings gave the results shown in the table below:

RO performances of resorcinol/formaldehyde-coated CA membranes

Formaldehyde: Resorcinol Ratio	Retention (%)		Flux (ℓmh)	
	Before	After	Before	After
0,45 : 1	62,26	80,90	45,74	30,33
	75,58	94,58	50,03	30,26
	84,78	95,26	32,23	25,20
0,52 : 1	60,08	91,44	58.23	33,56
	62,35	91,63	52,30	30.,73
	73,08	90,49	41,37	32,90
1,20 : 1	78,42	91,00	43,45	27,83

Different layers of coatings could be applied in succession without any loss in flux from the first regeneration through to the next. Membranes which had retentions in the region of 88,92% could be improved to 96,28% by two regenerations. The final retentions were maintained for the total test time of 350h.

3.4.3.2 Tannic Acid Treatment

This treatment had a marked effect on CA membrane performances. The salt retentions of the membranes were restored from initial values of 73,1 and 76,2% to 90,6 and 90,7%, respectively.

However, the effect on the flux performance was also marked: typical fluxes deteriorated from 29,1 and 25,0ℓmh to 20,7ℓmh. The treatment appeared stable and no further loss in performance was recorded after 650h testing.

3.4.3.3 Poly(acrylic acid) Treatment

The performance of CA membranes treated with this acid typically improved as follows:

Before coating:	74,6% and 43,5ℓmh
After coating:	88,0% and 34,1ℓmh

Although the fluxes of these membranes were still high enough for industrial use, the improvements in retention was considered to be insufficient to warrant further investigation.

3.4.3.4 Summary of Conclusions

Initial results have indicated the following:

Supplemental polymer treatment improves the salt-retention performances of membranes, at the cost of reduced water-flux.

The technique of membrane regeneration can be used to upgrade the performance of sub-standard membranes, or to prepare new membranes with improved properties.

The end-performance of the coated membranes depends on the materials with which they were coated, the coating's chemical formulation, conformation and molecular mass.

Coatings must be tailor-made according to the pore size distribution of the new membranes.

Circulation (*in situ*) treatment with a 50mg/l of resorcinol-formaldehyde resin is an effective means of regeneration.

Screening tests have been performed on laboratory scale. It is recommended that, in future, tests be performed on industrial scale with the resorcinol/formaldehyde coating.

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LIST OF ABBREVIATIONS

ABAKOR - South African Abattoir Corporation
API - American Petroleum Industry stream
AV - Average
BDA - Blowdown to ash
CA - Cellulose acetate
CAMOH - Code name for experimental UTF-RO membrane
CAMPIP - Code name for experimental UTF-RO membrane
CMC - Carboxy methyl cellulose
COD - Chemical oxygen demand
CTE - Cooling-tower evaporation
CWBD - Cooling-water blowdown
DSC - Differential scanning calorimetry
EDAX - Elemental diffraction analysis of x-rays
EDTA - Ethylene diamine tetra-acetic acid
e.g. - For example
ETP - Excess water to ponds
Eq. - Equation
FAPI - Fresh American Petroleum Industry stream
FF - Fresh-feed stream
Fig. - Figure
HOIPS - Code name for experimental UTF-RO membrane
IAWQ - International Association on Water Quality
ID - Inside diameter
i.e. - That is
IPC - Isophthaloyl chloride
IPS - Institute for Polymer Science
KHT - Potassium bitartrate
MEMTUF - Membratek tubular ultrafiltration
MF - Microfiltration
MM - Molecular mass
MMCO - Molecular mass cut-off
NF - Nanofiltration
PCW - Process cooling-water
PEG - Polyethylene glycol
PES - Poly(ether sulphone)
PIP - Piperazine
PRG - Pollution research group
PS - Polysulphone
PVAM - Polyvinylamidine (poly-2-vinylimidazoline)
PVC - Polyvinyl chloride

PVME	-	Polyvinyl methyl ether
PVOH	-	Polyvinyl alcohol
PWF	-	Pure-water flux
Ref.	-	Reference
RO	-	Reverse osmosis
RXW	-	Reaction water
SABS	-	South African Bureau of Standards
SCl	-	m-Sulphonyl benzoyl chloride
SEM	-	Scanning electron microscope
SGL	-	Stripped gas-liquor
SS	-	Suspendid solids
SWUF	-	Seawater ultrafiltration
TAB	-	3,3'-4,4'-biphenyl-tetramine
TDS	-	Total dissolved solids
Temp.	-	Temperature
TEA	-	Triethylamine
TMC	-	Trimesoyl chloride
TRO	-	Tubular reverse osmosis
TSP	-	Trisodium-o-phosphate
TSS	-	Total suspendid solids
UF	-	Ultrafiltration
uPVC	-	Unplasticised polyvinyl chloride
UTF	-	Ultra-thin-film
WRC	-	Water Research Commission

LIST OF SYMBOLS

°C - degrees Celsius
g - gram(s)
g/l - gram per litre
h - hour
kg - kilogram(s)
kg/h - kilogram per hour
kg/MJ - kilogram per megajoule
kPa - kilopascal
l - litre
l/h - litre per hour
lmd - litres per square metre per day
lmh - litres per square metre per hour
l/min - litre per minute
m - metre
m^2 - square metre
m^3/d - cubic metre per day
mg/l - milligram per litre
ml - millilitre
ml/l - millilitre per litre
mm - millimetre
m/s - metre per second
µm - micrometre
min - minute
MJ - megajoule
MPa - megapascal
% - percentage
pH - inverse log of concentration of protons in solution
ppm - parts per million

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Membrane separation technology resulted from a single event: the development of the synthetic asymmetric membrane in 1960 at the University of California, Los Angeles, by Sourirajan and Loeb [Ref. 1.1]. Since then it has spawned a vast array of diverse applications almost unmatched by any other separation process. Desalination and water treatment by RO are probably the earliest and best known applications.

RO is essentially a dewatering process, whereas UF is a fractionation technique that can simultaneously concentrate macromolecules or colloidal substances in process streams.

The general advantages of separations by membrane systems include:

(i) simple design of membrane systems;

(ii) membranes are modular in nature, making expansion of the system easy;

(iii) membrane systems are readily adaptable to changes in quality of feed streams;

(iv) membrane systems often use less energy than conventional treatment systems do; and

(v) membrane systems have potentially lower capital and operating costs than conventional treatment systems do [Ref. 1.2].

1.2 OBJECTIVES

1.2.1 GENERAL

In this study various experimental and established membranes and membrane systems were to be tested on various industrial effluents. Ultrafiltration, reverse osmosis and nanofiltration membranes were to be used in various applications. Research was also to be done on aspects such as the cleaning of severely fouled membranes, membrane production quality control and process development.

The objectives of this study were:

(i) the on-site testing of established UF, RO and NF membranes in industrial applications;

(ii) evaluation of experimental membranes to determine any possible shortcomings;

(iii) the installation and evaluation of new membranes which became available through research on industrial effluents;

(iv) address problems associated with membrane processes and operation, for example, cleaning of fouled membranes and membrane performance restoration;

(v) address problems in existing membrane systems by using experimental membranes with different physical properties, and the investigation of the use of various pretreatment methods;

(vi) the design, construction and installation of test equipment for the above applications, as necessary; and

(vii) studying the regeneration chemistry for CA membranes to establish an acceptable and effective regeneration procedure.

1.2.2 MOTIVATIONS FOR SPECIFIC MEMBRANE APPLICATIONS INVESTIGATED

1.2.2.1 UTF RO membranes for brackwater treatment

Membratek, a local company that specializes in the manufacture of a variety of membranes and membrane systems, informed the Institute of Polymer Science of an opportunity to test experimental IPS RO membranes on-site in Botswana. The goal of the operation was to desalinate brackish water to a potable standard, complying with SABS specifications. While Membratek would install their conventional CA RO membranes, IPS would provide alternate experimental ultra-thin-film RO membranes. These membranes had first to be potted into 1,2 m modules by Membratek before installation at the test-site. The IPS membranes were first to be manufactured on a small scale and tested; then selected membranes were to be manufactured on a larger scale. Batch tests were to be performed on them before they were sent to Membratek for potting in modules.

1.2.2.2 Treatment of cooling water blowdown with membrane processes

In industry, in a closed system, a general increase in salt and organic concentrations is inevitable. Scaling occurs in equipment and valves because of the salt build-up, while fouling results from the presence of organic substances and suspended solids in the effluent. These problems can be reduced by bleeding a constant stream of effluent to evaporation ponds or by using it for ash consolidation. This is, however, not the ideal solution because of the high cost involved and the limited space available for building evaporation dams.

The following questions must be asked when problems arise in industrial effluent treatment:

(i) Is an alternative method of treatment possible?

(ii) Where in the system does the highest salt and organic concentration exist?

(iii) Which method would potentially be the most suitable for solving the specific problem?

The improvement of the quality of effluent recycled within the system would result in a decrease in external water intake. The salt and organic concentrations of wastewater could be increased thereby. This would result in more effective discharge of water to evaporation ponds.

UF and RO membranes were to be tested on Sasol effluent. Cooling-water blowdown (CWBD) was selected as the most suitable stream for testing the membranes because of the fact that this effluent contained a variety of dissolved and suspended organic and inorganic solids. The idea was to remove most of the suspended solids and macromolecular substances in the effluent by UF, while RO would be applied for salt removal.

Established as well as experimental membranes were tested first on a laboratory scale at the IPS laboratories on Sasol cooling-water blowdown. Because the effluent underwent chemical changes when stored for a period of time, it was of great importance to always work with a fresh effluent in order to simulate true operating conditions during evaluation. After extensive in-house evaluation it was subsequently decided to rather test the membranes on-site at Secunda to achieve more reliable results. Three test-rigs were designed and constructed for installing at Sasol. Sasol undertook to maintain the test equipment and to supply IPS with the necessary test data on a regular basis. Tubular UF membranes, capillary UF membranes, NF membranes and various RO membranes were tested on-site on CWBD. This investigation supplied valuable information regarding the performance of experimental membranes and practical operation problems could be identified.

1.2.2.3 Potassium bitartrate recovery from wine rests with membranes

The main objective of this study was to determine whether membrane processes could be applied to the fractionation of wine lees to produce useful by-products such as yeast cells, cream of tartar and proteins. A most important by-product of wine lees is potassium bitartrate (KHT), the reason being that it is expensive to import. The colloids and macromolecules in the wine lees could be separated by UF, while RO could be used to concentrate KHT which passes through the UF membranes. For the purpose of the study, wine lees was provided by a company which specializes in the extraction of KHT from wine lees which they collect from wine cellars. After a period of testing, a NF pilot plant was installed at the factory; this provided valuable results regarding experimental NF membranes.

For the purpose of this study, UF membranes were used in diafiltration mode to "wash" the wine lees slurry at different solids concentrations. The KHT-rich permeate collected from UF was then concentrated using RO and NF to allow subsequent precipitation of the product.

1.2.2.4 Restoration of membrane performances

As the economic viability of a membrane operation is dependant on adequate membrane performance, it is of great importance to be able to restore the performances of membranes which, with time, may have fallen to below acceptable levels.

This was to be investigated from two angles:

1. Cleaning regimes.
2. Membrane regeneration by application of supplemental coatings.

Firstly, various cleaning methods for various membranes, used in various applications, were to be investigated. Emphasis was to be placed on the development of a suitable cleaning regime for UF membranes used in the treatment of (i) an abattoir effluent and ii) seawater pretreatment for RO desalination.

Secondly, the suitability and effectiveness of employing various supplemental polymer coatings to regenerate substandard cellulose acetate (CA) membranes was to be investigated.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 WATER PURIFICATION

Although water covers some 70% of the surface of the earth, only a very small percentage is available for use by man, either directly or after simple treatment [Ref. 2.1]. Water is a good solvent, and hence very pure water is rarely found in nature. Impurities are present in water in three progressively finer states - suspended, colloidal and dissolved. Different treatment methods are required to reduce their levels to the required values.

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 hardship of periodic droughts. Present groundwater resources in South Africa are estimated to be adequate for only the next 30 years, whereafter demand will exceed supply [Ref. 2.1].

Although water treatment processes are usually used to produce potable water, they may also be used to treat industrial feed-water and industrial effluents. As water consumption for domestic and industrial purposes increases, the quantity of treated effluent entering into the environment increases. This means that an even larger percentage of our raw water supplies consist of "second-hand" water. In the lower reaches of the Vaal/Orange river system, the water has, on average, been used seven times [Ref. 2.1]. This indicates that in future great emphasis will have to be placed on water treatment and water purification methods.

2.2 PRESSURE-DRIVEN MEMBRANE OPERATIONS

A synthetic membrane is a porous or dense-porous film which exhibits selective transport properties under the influence of an external driving force, that is, the primary role of a membrane is to act as a selective barrier. This means that a membrane has the ability to retain certain dissolved species present in a water stream, while allowing water to pass through under the action of pressure as the driving force.

In the case of membranes that operate according to "sieving" mechanisms, such as microfiltration (MF) and ultrafiltration (UF), pressure is utilized as the driving force. In this case, the water is forced through the pores in the skin of the membrane, whereas the dissolved and the suspended matter is retained according to their size in relation to that of the pores in the membrane. However, UF and MF membranes do not retain salt. In the case of nanofiltraion (NF) and reverse osmosis (RO) operations, pressure is also utilized as the driving force, although the mechanism according to which separation is effected, differs from that of UF and MF membranes. (Other driving forces utilized in membranes systems are concentration gradient as in the case of dialysis, and an electrical potential gradient as utilized in the case of electrodialysis.)

Membranes are available in two basic configurations, namely, tubular and flat-sheet. These membrane are usually manufactured by wet-phase inversion when a polymer, for example, polysulphone, is cast upon a reinforcing fabric (Fig. 2.1).

The large-diameter tubular membranes are particularly attractive when used in the treatment of wastewater. The reason for this is that suspended solids are free to pass through the tubes without a great risk of causing blockage of the tube entrances. Another important factor in favour of the tubular configuration is that the tubular membranes can also be cleaned by mechanical methods such as sponge ball swabbing.

The capillary (Fig. 2.2) and hollow-fibre membranes and the flat-sheet configurations (i.e., spiral-wound configurations) are attractive for their high membrane area-to-volume packing densities. Other advantages of the capillary configuration is that it is self-supporting; drag-force-to-pump energy ratios are higher than with tubular membranes, and a relatively low module cost is achieved. However, the disadvantage of this system is that the maximum particle size in the effluent stream may not exceed the inside diameter of the capillary membrane, as this would result in blockage of the capillary entrance resulting in a reduction in effective membrane area. Mechanical cleaning of capillary membranes is virtually impossible, and therefore enzymatic soap washes, chemical treatment, pH treatment, ultrasonic treatment and backwashing are the only alternatives for restoring permeate flux when membrane fouling has occurred.

Figure 2.3 shows a classification of various separation processes based on particle or molecular size, and the primary factors affecting the separation process [Ref. 1.1]. The five major membrane separation processes, that is, reverse osmosis, ultrafiltration, microfiltration, dialysis and electrodialysis, cover a wide size-range. The real worth of membrane processes is that they permit separation of dissolved species of sizes down to the ionic range, provided the appropriate membrane operation is used.

What distinguishes the more common membrane operations, MF, RO and UF, is the application of hydraulic pressure to effect solvent and solute transport through the membrane (Fig. 2.4). However, it is the nature of the membrane itself which controls which component permeates and which component is retained. Ideally, in RO all components other than the solvent itself are retained, whereas in UF only macromolecules or particles larger than approximately 0,001 μm are retained [Ref. 1.1]. MF processes, on the other hand, are designed to retain particles in the "micron" range, that is, suspended particles in the 0,1 μm to about 10 μm size-range.

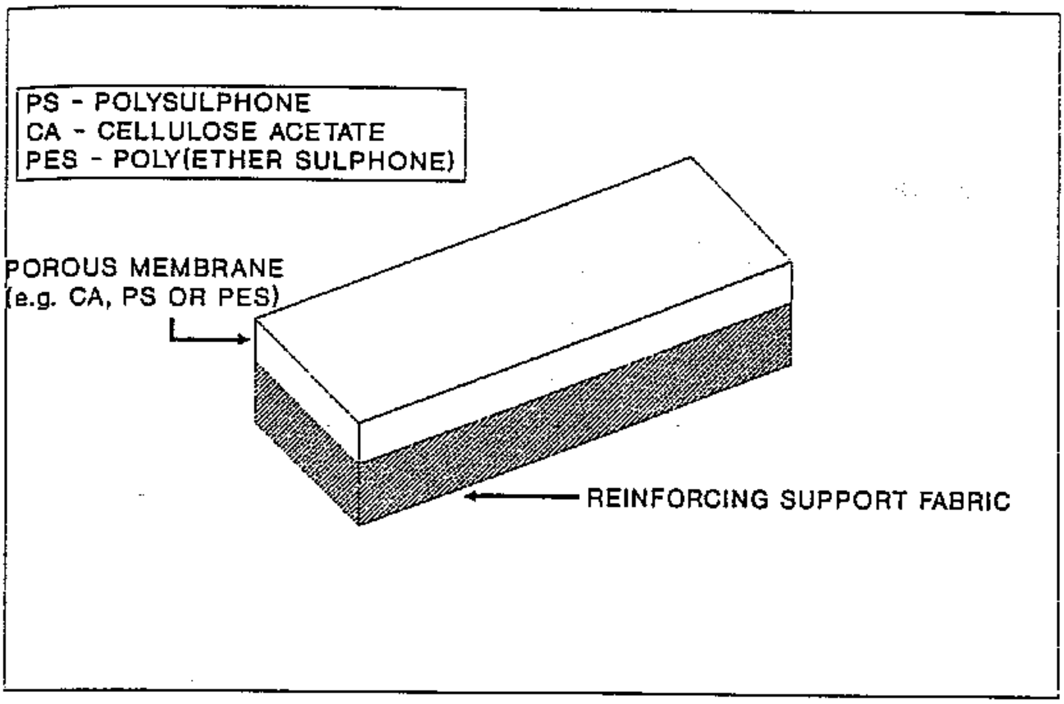
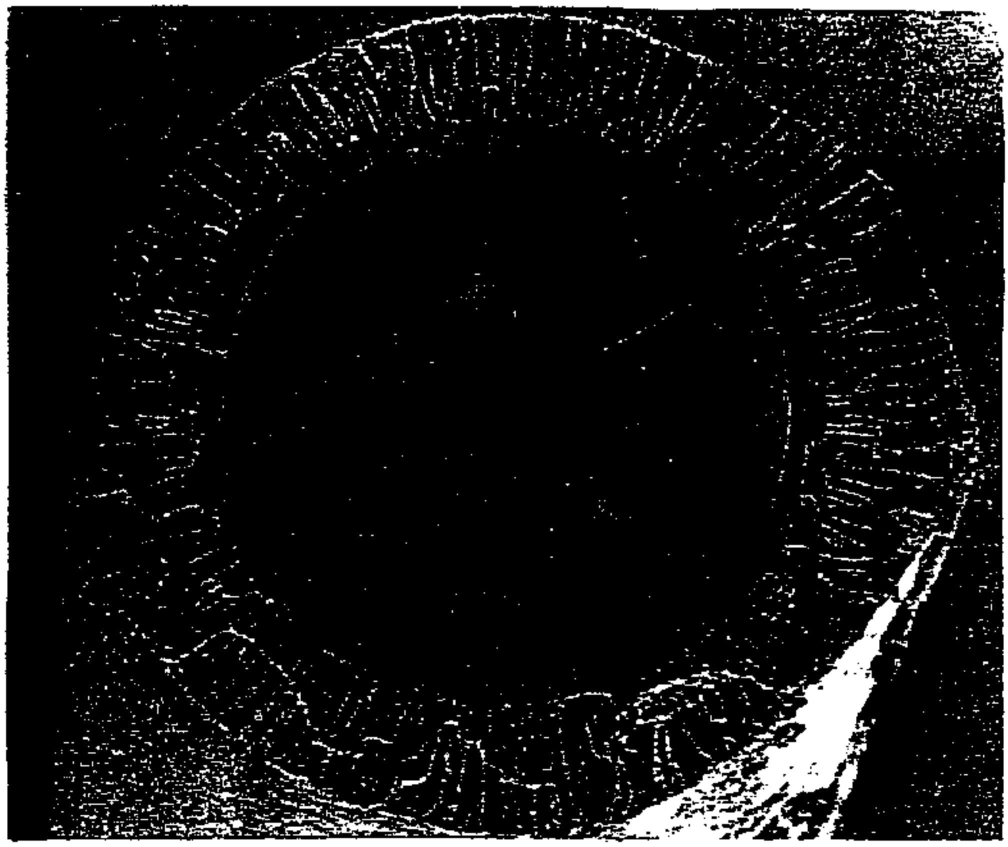


Fig. 2.1:
Cross-section of a tubular or flat-sheet membrane.



Courtesy of WRC project

Fig. 2.2:
A SEM photograph of the cross-section of a capillary UF membrane.

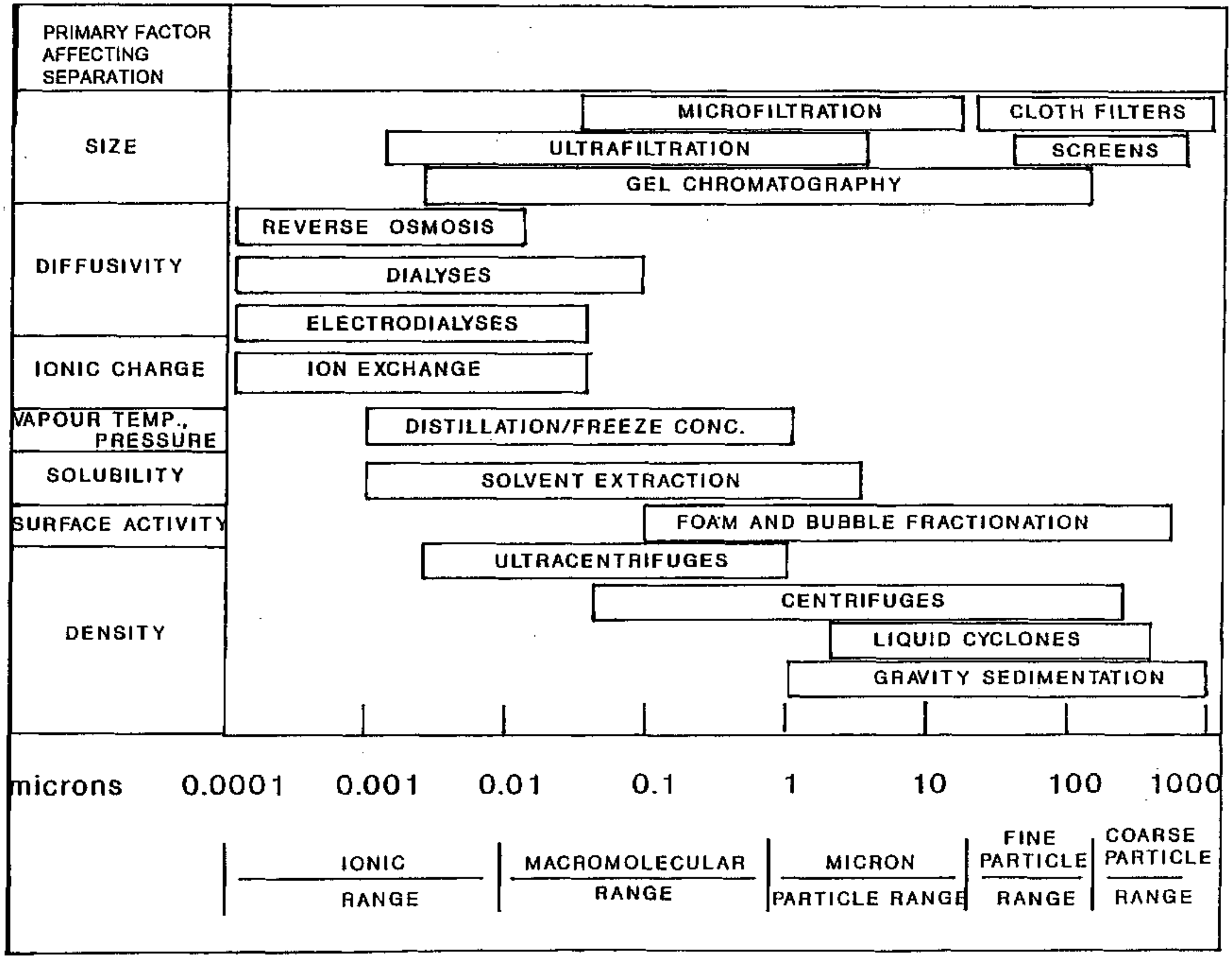


Fig. 2.3:
Useful range of separation processes, showing the range of particle or molecular size covered by each process, and the primary factor governing each separation process.

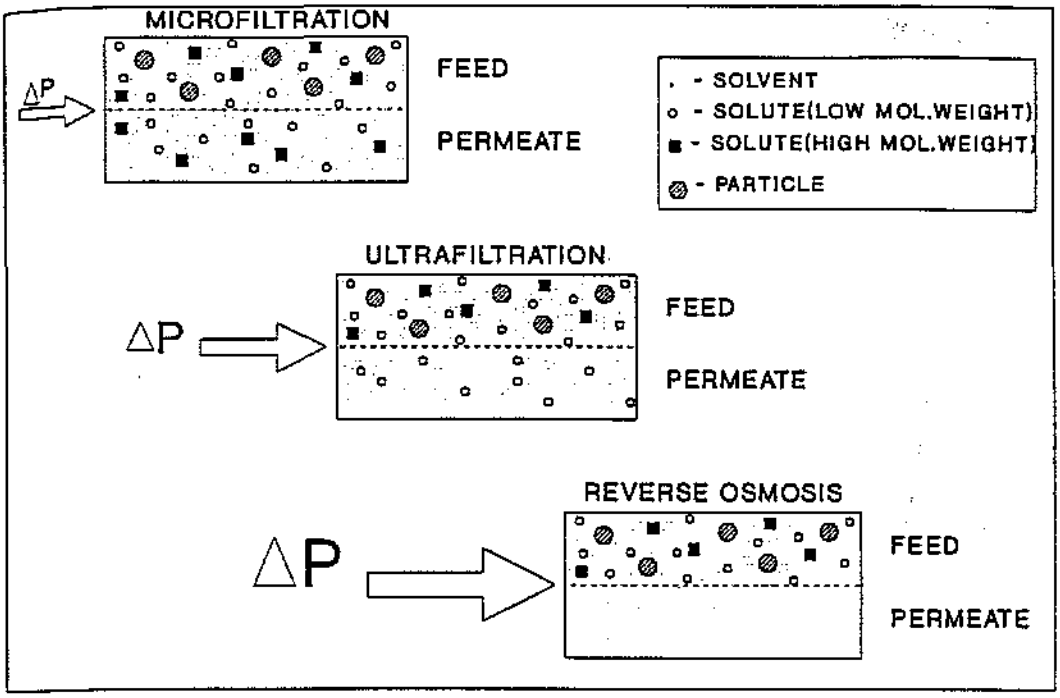


Fig. 2.4:
Schematic representation of microfiltration, ultrafiltration and reverse osmosis separation operations.

In conventional usage, particles larger than 10 μm are best separated by conventional filtration processes such as coagulation followed by sand filtration, for example. However, in comparison, RO is essentially a dewatering technique, while UF can be regarded as a method for simultaneously purifying, concentrating and fractionating macromolecules or fine colloidal suspensions.

CHAPTER 3

MANUFACTURE OF TUBULAR UTF RO MEMBRANES FOR BRACKWATER TREATMENT

3.1 BACKGROUND

Prompted by a suggestion from Membratek, the steering committee supported the move to investigate the suitability of selected IPS tubular UTF-RO membranes for desalination of a feed water from Botswana which had a TDS of approximately 3 000 mg/l and a temperature of up to 38°C.

The standards with which the membranes were to comply were that the membranes should have a high retention (90% NaCl) and be able to operate at relatively low pressures (2-3 MPa) with sponge-ball cleaning and flow reversal. Membratek would install their standard CA RO membranes for evaluation while IPS would have the opportunity to submit their experimental tubular ultra-thin-film (UTF) RO membranes. These membranes were to be potted into 1,2 m modules by Membratek before installation at the site in Botswana.

Experimental UTF-RO CAMOH and CAMPIP membranes which had previously been manufactured and tested in flat-sheet and tubular configurations during a parallel project at IPS (Tolerant Membranes, Project no. 219), as described by M.J. Hurndall [Refs. 3.1 to 3.4], were amongst those selected for application.

Other membranes selected were those also investigated as part of a Tolerant Membranes Project (No. 361), the PVOH-based membranes.

3.2 OBJECTIVES

The objectives of the study were to:

(i) manufacture 1,2 m lengths of tubular UTF-RO membranes (codes: CAMOH, CAMPIP and FURFURYL ALCOHOL/ ISOPROPANOL);

(ii) produce 1,2 m lengths of PVOH-RO membranes (HOIPS);

(iii) evaluate the above-mentioned membranes in the laboratory to determine whether they complied with the required standards;

(iv) select membranes, scale-up their production and re-evaluate them; and

(v) supply Membratek with sufficient tubular membranes, of requested standards, to enable them to produce eight modules, each 1,2 m long (19 membranes per module).

3.3 EXPERIMENTAL

3.3.1 MANUFACTURE OF MEMBRANES

3.3.1.1 PVOH RO membranes - HOIPS

A commercial 719 UF membrane developed at IPS (1988) and supplied by Membratek, was used as substrate membrane. The membranes were first dipped into an aqueous solution of polyvinyl alcohol (PVOH), piperazine (PIP) and NaOH (N_x-codes in the table below). After draining it for a certain period of time, the membranes were again dipped into an isophthaloyl chloride (IPC) or trimesoyl chloride (TMC) in hexane solution to effect crosslinking (X_x-codes in table below). The membranes were drained again and cured at 110 °C for a period of 10 minutes.

Two of each of the following membranes were manufactured:

N_1X_1	N_1X_2	N_1X_3
N_2X_1	N_2X_2	N_2X_3
N_3X_1	N_3X_2	N_3X_3
N_4X_1	N_4X_2	N_4X_3
M_1X_1		M_1X_3
M_2X_1		M_2X_3
M_3X_1		M_3X_3

Where N_1: 0,25 PVOH + 0,25 PIP + 0,5 NaOH (aqueous phase)

N_2: 0,5 PVOH + 0,5 PIP + 0,95 NaOH (aqueous phase)

N_3: 0,5 PVOH + 0,45 PIP + 0,05 TAB + 0,95 NaOH (aqueous phase)

N_4: 0,5 PVOH + 0,45 PIP + 0,05 CPA + 0,95 NaOH (aqueous phase)

$M \equiv N$ but manufacturing conditions differ.

and X_1: 1% IPC in hexane

X_2: 1% TMC in hexane

X_3: 2% TMC in hexane

3.3.1.2 PVOH-RO membranes - CAMOH and CAMPIP

In the fabrication of CAMOH and CAMPIP membranes the Membratek commercial polysulphone substrate (code 719) was used. Membranes were dipped in an aqueous solution of triethylamine (TEA), trisodium orthophosphate (TSP), polyvinylamidine (PVAM) and piperazine (PIP) (in the case of CAMPIP) or PVOH (in the case of CAMOH). The membranes were then drained for a period of time and dipped into a hexane solution of m-sulphonyl benzoyl chloride (SCl) to effect crosslinking. The membranes were again drained prior to heat curing in an oven at approximately 100 °C for 10 minutes.

Two of each of the following membranes were made:

CAMPIP 3:	PVAM	-	1,08%
	PIP	-	0,12%
	TEA	-	0,2%
	TSP	-	0,5%
CAMOH 5:	PVAM	-	0,96%
	PVOH	-	0,24%
	TEA	-	0,2%
	TSP	-	0,5%

Crosslinking solution for CAMPIP 3 and CAMOH 5: 3% SCl in hexane.

3.3.1.3 PVOH-RO membranes - furfuryl alcohol/isopropanol

The commercial 719 UF membrane was again used as substrate. The membranes were dipped in the aqueous solution described below, drained and baked at temperatures between 130°C and 150°C.

Three each of the following furfuryl alcohol/isopropanol membranes were manufactured:

codes F_1LT and F_1HT

Where	F_1:	PVOH (15M)	-	1%
		Isopropanol	-	20%
		H_2O	-	75%
		H_2SO_4	-	2%
		Furfuryl alcohol	-	2%
	LT	Cured at 130 °C		
	HT	Cured at 150 °C		

3.3.2 MEMBRANE TEST RESULTS

All membranes were tested on a 2 000 ppm NaCl feed solution at 30 bar operating pressure, a linear fluid flow velocity of 1,5 m/s and at 20 °C.

3.3.2.1 HOIPS membranes

Results of HOIPS membranes are illustrated in Figure 3.1; fluxes and retentions varied widely from one membrane type to another. The best results were obtained with membranes N_1X_1 and M_1X_1 with fluxes ranging from 20 to 30 lmh with corresponding NaCl retentions ranging from 78 to 84%.

3.3.2.2 CAMOH and CAMPIP membranes

As shown in Figure 3.2, generally good results were obtained from the CAMOH and CAMPIP membranes; permeate fluxes ranged from 15 to 40 lmh and corresponding retentions were above 90%. The membranes were then dried out over a period of two weeks to determine whether dry storage was possible, and tested again under the same conditions. The results (Fig. 3.3) showed reductions in both permeate flux and retention when the membranes were dried out. While the retention recovered to a certain extent, to the previous level of 90%, the flux-values remained low. From this it appears that the membranes should be stored in water before being potted into modules and should not be allowed to dry out for prolonged periods of time.

3.3.2.3 Furfuryl alcohol/isopropanol membranes

Figure 3.4 shows that these membranes were not efficient when manufactured as tubular membranes. The membranes were very brittle and had to be handled with great care to prevent their cracking. Another problem was that the tubular membrane support fabric could not withstand the high temperatures at which the membranes were baked, and degradation was evident in certain regions of the support fabric.

3.3.2.4 Discussion

The best-performing membranes were selected for manufacture on a larger scale (eight 1,2 m-long modules). It was decided to manufacture the N_1X_1 (HOIPS), CAMOH 5 and CAMPIP 3 membranes. Random batches of the membranes were retested and adequate RO performance results indicated that manufacture on the larger scale was successful. The membranes were then stored in a weak, aqueous formaldehyde solution prior to sending them to Membratek for potting into modules.

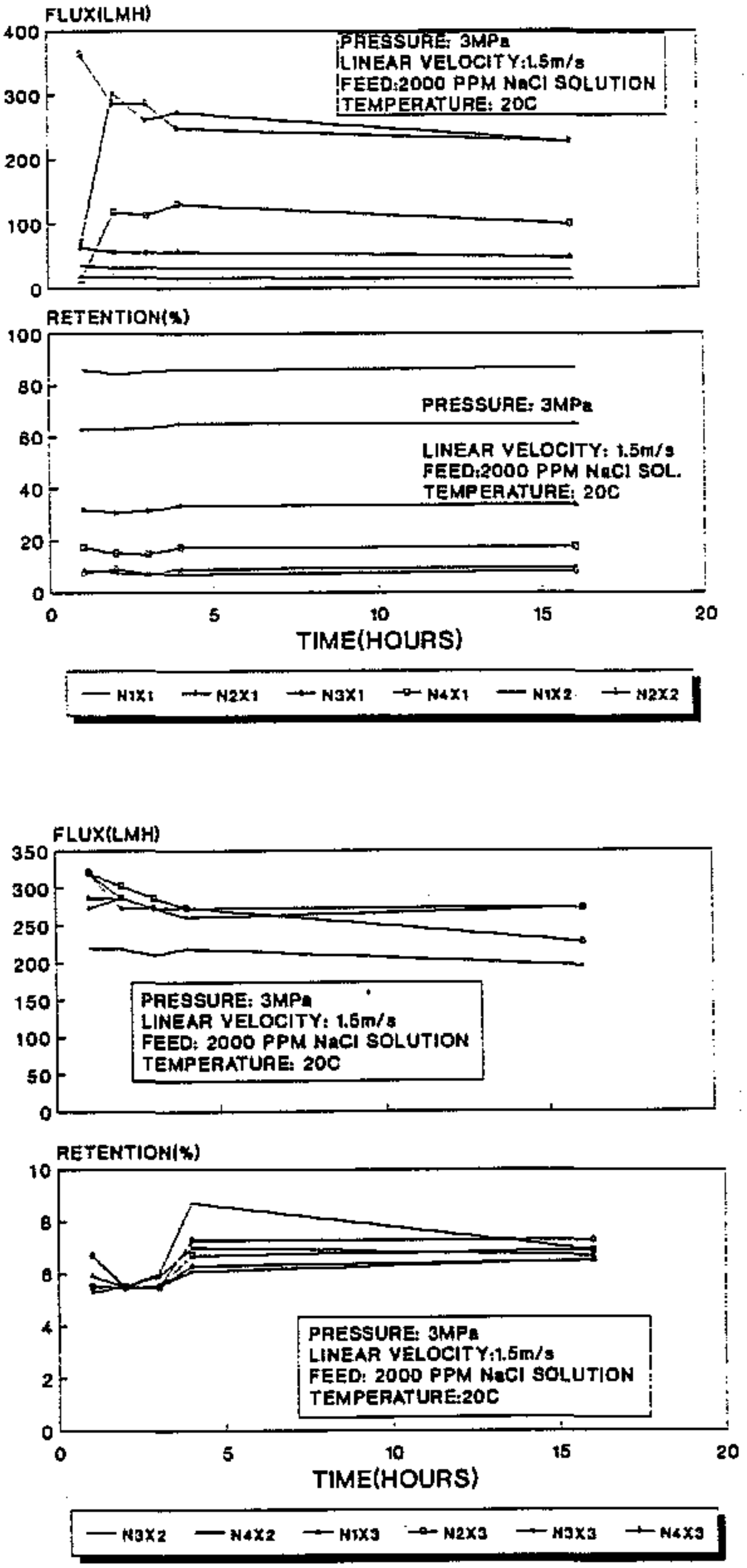


Fig. 3.1:
Flux and retention performance of HOIPS membranes tested on a 2 000 ppm NaCl feed solution.

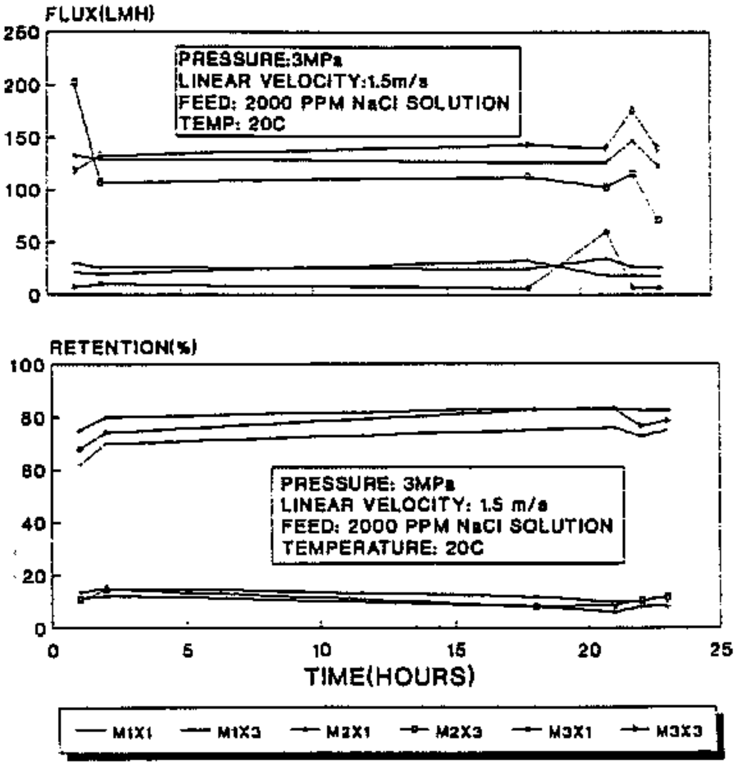


Fig. 3.1:(continued)
Flux and retention performance of HOIPS membranes tested on a 2 000 ppm NaCl feed solution.

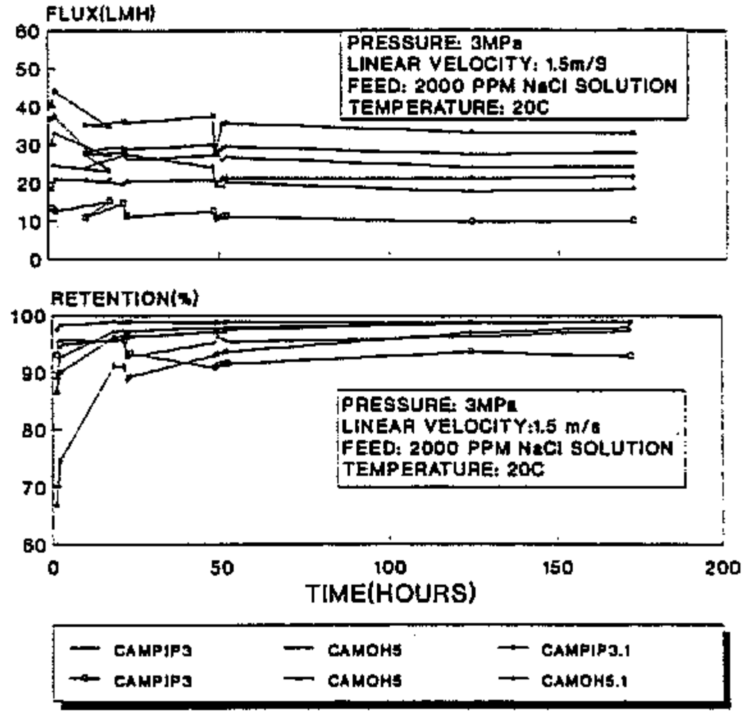


Fig. 3.2:
Flux and retention performance of CAMOH and CAMPIP membranes tested on a 2 000 ppm NaCl feed solution.

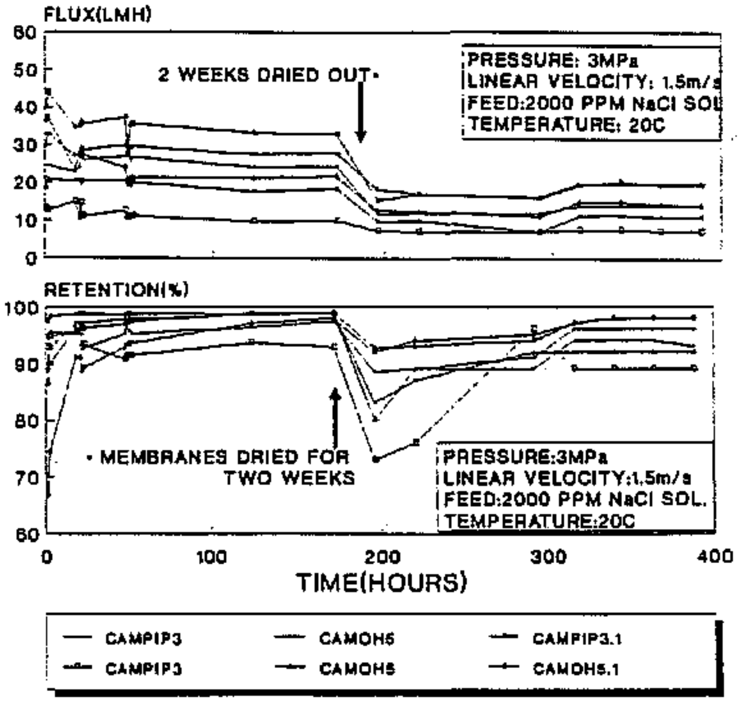


Fig. 3.3:
Flux and retention performance of CAMOH and CAMPIP membranes tested on a 2 000 ppm NaCl feed solution, after allowing the membranes to dry out for two weeks.

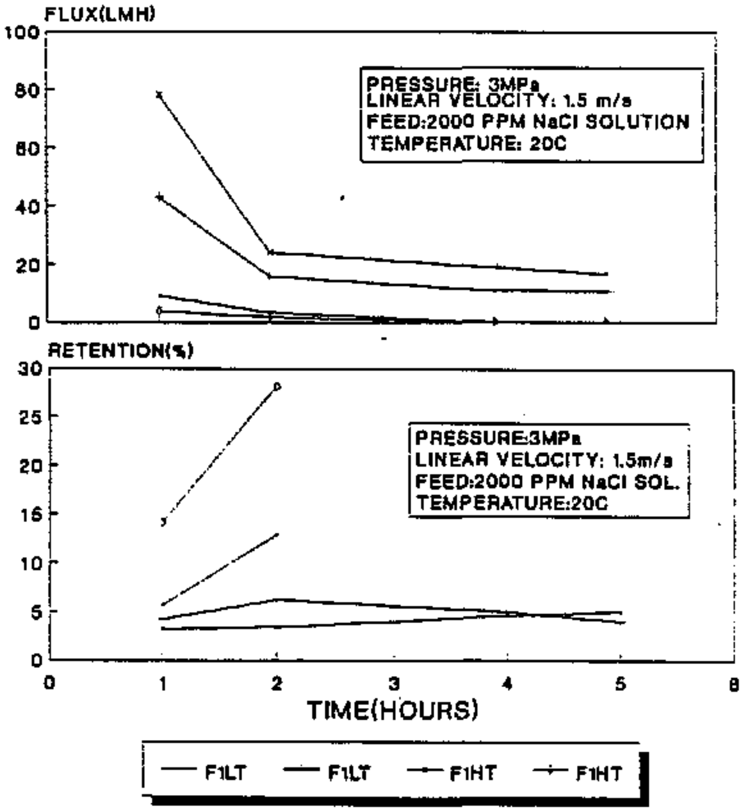


Fig. 3.4:
Flux and retention performance of FURFURYL ALCOHOL/ISOPROPANOL membranes tested on a 2 000 ppm NaCl feed solution.

3.3.3 QUANTITY FABRICATION OF MEMBRANES AND MODULE-MAKING

Selected membranes were produced on a larger scale and batch-tested at regular intervals. Generally, similar test results to those of the previous small-scale experiment were obtained. In cases, even higher retentions were obtained; CAMOH and CAMPIP membranes gave 99% retention (Fig. 3.5). The CAMPIP membranes also gave exceptionally high flux-values (average of 65 lmh), with correspondingly good average retention-values of 99%. The membranes were stored in a weak aqueous formaldehyde solution for three days, and again batch-tested to see whether this treatment had any effect on membrane performance. No significant difference in performance was evident, and the membranes were regarded as fit for incorporation into modules.

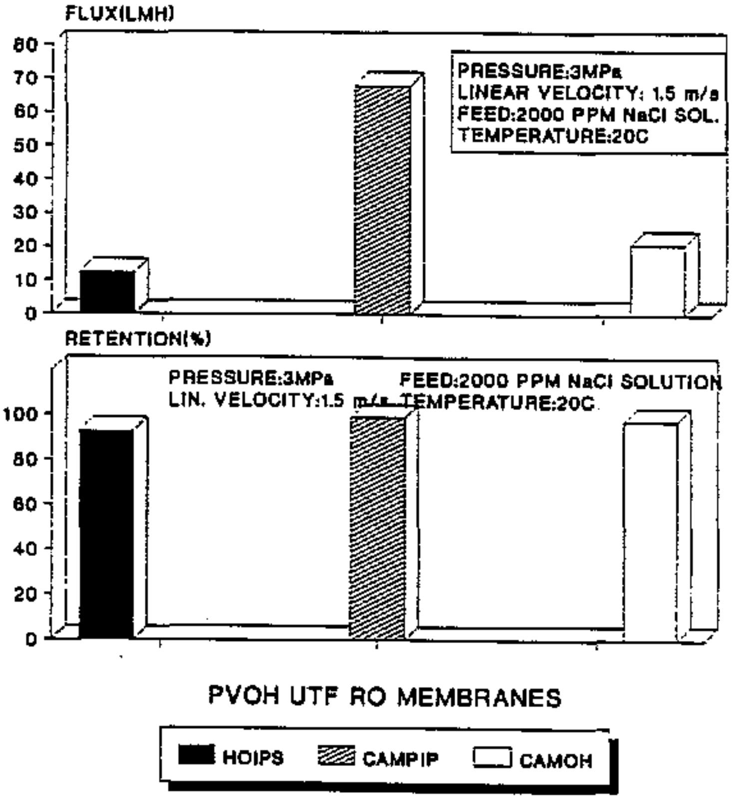


Fig. 3.5:
Flux and retention performance of HOIPS, CAMPIP and CAMOH membranes (produced on a large scale) tested on a 2 000 ppm NaCl feed solution.

The membranes were again subjected to a standardization test after they had been potted into modules. It was then found that both the fluxes of membranes and their retention values had dropped to unaccceptable levels.

It was decided to dry out some of the original membranes for a period of 30 days to determine to what extent this would affect membrane performance. This was done because it was thought that a possible reason for the poor performance of the membranes in the modules was that the membranes had been allowed to dry out during the potting process. Membranes were also taken from the modules and tested in separate test cells as controls. These results were compared with the membrane test results collected after original membrane fabrication. Figures 3.6 to 3.8 show only a slight reduction in flux after a drying period of one month. The membranes which were potted into modules, without exception, showed a marked reduction in retention and a corresponding increase in flux.

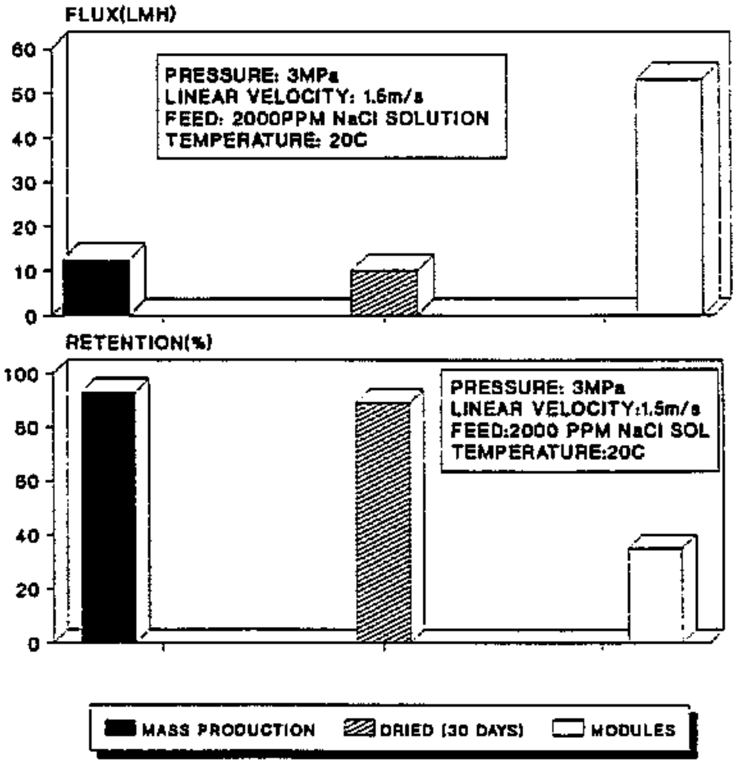


Fig. 3.6:
Comparison of HOIPS membrane performance after: (a) quantity fabrication, (b) a drying period of one month, and (c) incorporation into modules.

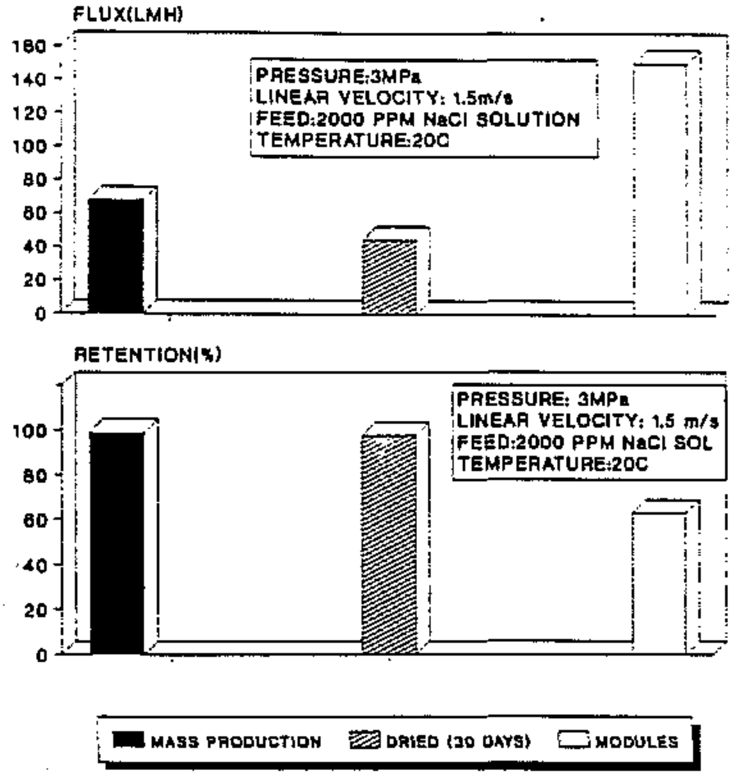


Fig. 3.7:
Comparison of CAMPIP membrane performance after: (a) quantity fabrication, (b) a drying period of one month, and (c) incorporation into modules.

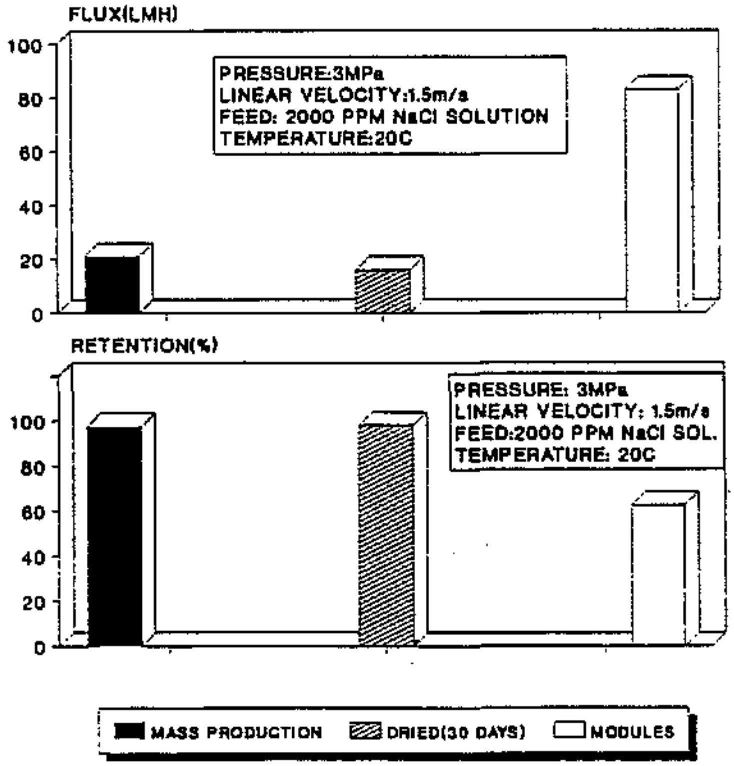


Fig. 3.8:
Comparison of CAMOH membrane performance after: (a) quantity fabrication, (b) a drying period of one month, and (c) incorporation into modules.

3.4 DISCUSSION

Inadequate membrane performance was recorded for all three types of membranes after they had been incorporated into modules.

The following may be a reason for the poor performance of membranes after being subjected to treatment associated with the module-making process. During the experimental work it became clear that UTF membranes should be handled with extreme care to prevent damage to the ultra-thin film on the support. During the potting process it is difficult to handle the membranes with the necessary care and it is therefore possible that the membranes could have been damaged during module making. It must be remembered that only short lengths of experimental UTF mebranes were handled during bench evaluation studies. However, during module preparation longer lengths of these membranes were handled and therefore the tubes were more susceptible to flexing and possible subsequent damage to the UTF membrane layer.

3.5 CONCLUSIONS AND RECOMMENDATIONS

Ways to minimize damage during module-making should receive further attention. A possible solution for this problem could be the use of a double-wound support fabric to reduce bending of the tube during handling.

Alternate and perhaps more suitable methods for storing these UTF-RO membranes, should also be considered. Results of storage experiments of PVAM membranes, carried out during an earlier IPS project [Ref. 3.5], should be considered and applied here.

Although the "applications project" has been terminated, due to the occurance of the abovementioned problem, these investigations will continue as part of another WRC project at IPS, namely the Tolerant Membranes Project (1994-1996).

CHAPTER 4

TREATMENT OF SASOL COOLING-WATER BLOWDOWN

4.1 BACKGROUND

The quality of the process cooling-water (PCW) in the Sasol II and III works had deteriorated in the past few years, due to an increase in salinity and other contaminants. This PCW stream is an intermediate stream which is continuously upgraded during the process. Table 4.1 illustrates the different problems caused by a variety of components in the effluent. The evaluation of potential solutions to this problem, in particular the reduction of levels of scale-forming ions such as fluorides, sulphates and calcium, required high priority.

The greater PCW system is shown in Figure 4.1. The main streams into the system are stripped gas-liquor (SGL), reaction water (RXW), and a stream combining all new waters which enter the system via the API-stream. The main streams leaving the system are cooling-tower evaporation (CTE), blowdown to ash (BDA) and excess water to ponds (ETP) for storage. The fresh-feed stream (FF) is a hypothetical one and is a combination of the three streams bringing fresh contaminants into the PCW system, namely, FAPI, SGL and RXW.

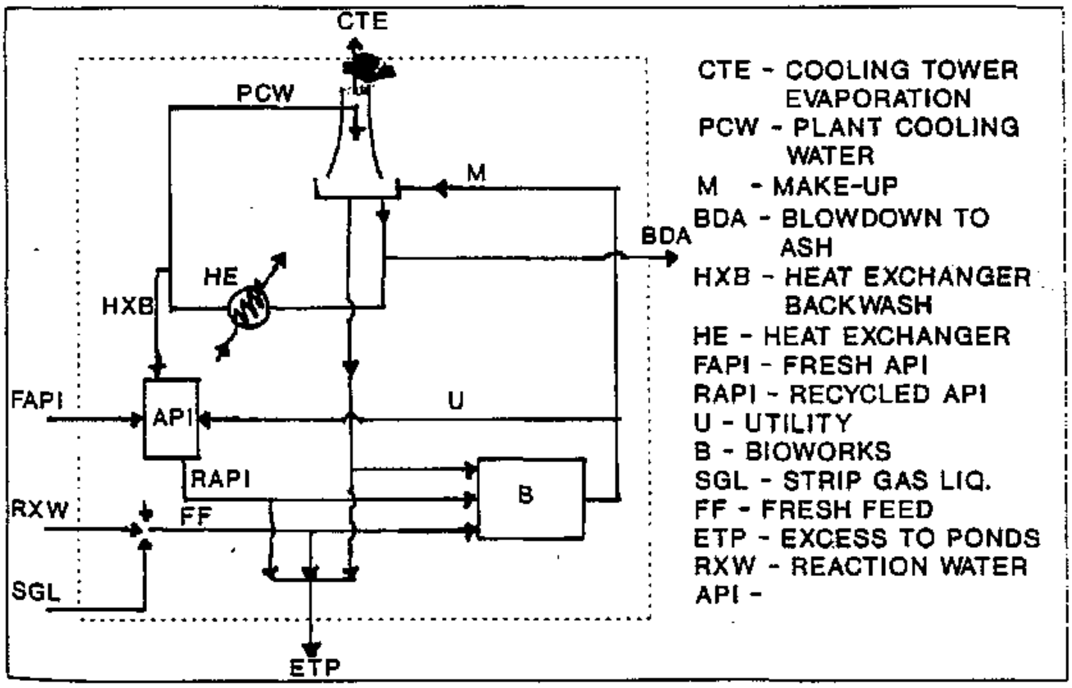


Fig. 4.1:
Process cooling-water system at Sasol II and III.

The following general conclusions can be drawn with regard to the quality of process cooling-water over the past five years:

(i) The quality of PCW has deteriorated over a period of time. Specifically, the levels of sodium, chlorides, sulphates, chemical oxygen demand (COD), and total suspended solids (TSS), have increased by between 50% and 150%.

(ii) Fluoride levels have increased by approximately 12% but stabilized in the past two years, probably due to precipitation.

(iii) Total hardness levels have decreased over the past two years and are now lower than five years ago.

(iv) It is important to note that PCW quality shows a strong seasonal variation. Contaminant levels can range from 50% to 100% higher in the dry season than in the wet season, whereas total hardness, follows an inverse pattern.

Various components of the CWBD cause various problems. These have been summarised in Table 4.1.

Table 4.1: Components in CWBD and related problems

		ASSOCIATED PROBLEMS		
CONTAMINANT	**SYMBOL**	**FOULING**	**SCALING**	**CORROSION**
SUSPENDED SOLIDS	SS	■■		
CHEMICAL OXYGEN DEMAND	COD	■■		■
AMMONIA	NH_3	■		■
PHOSPHATES	PO_4^{3-}	■	■	■
FLUORIDES	F^-		■■	
SULPHATES	SO_4^{2-}		■	■■
CALCIUM	Ca^{2+}		■■	
CHLORIDES	Cl^-			■
SILICA	SiO_2		■■	
ALUMINA	Al_2O_3		■■	

■■ Major influence ■ Minor influence

It was decided to test IPS UF and RO membranes on SASOL cooling-water blowdown. CWBD was sent regularly to Stellenbosch in 200 l drums. Various membranes were tested on this effluent. After extensive testing of tubular UF, capillary UF and PVOH NF membranes it was decided that test rigs should be designed and constructed to test these membranes on-site on a continuous stream of cooling-water blowdown.

4.2 OBJECTIVES

These were to:

(i) decrease salt and organic concentrations in the CWBD;

(ii) test and evaluate tubular IPS UF membranes on CWBD as a posssible means for pretreatment prior to RO;

(iii) gain information on experimental IPS NF and RO tubular membranes;

(iv) test experimental IPS UF capillary membranes;

(v) establish problems associated with membrane application; and

(vi) determine to what degree different concentrations of the effluent affect the membranes.

Different industrial effluents have different chemical compositions and therefore behave differently to membrane treatment. In the case of the Sasol CWBD effluent the challenge to adequately recover water to the extent that it meets the desired standards for re-use, using pressure-driven membrane systems, was hampered by the fact that the effluent contained a series of hydrophobic organic constituents which cause extensive fouling of the membrane surfaces. Permanent fouling could be prevented by means of regular detergent washes. Use of a UF membrane which exhibits hydrophilic properties may help to combat fouling.

4.3 EXPERIMENTAL

Tubular UF membranes as well as capillary UF membranes were tested on Sasol cooling-water blowdown. The tubular UF membranes included membranes with various MM cut-off values (Table 4.2). At this stage the capillary UF membranes were in a very early stage of development, and were, as yet, not characterized with regard to molecular mass cut-off (MMCO).

Table 4.2: Molecular mass cut-offs of different IPS tubular UF membranes

IPS Membrane code	PEG molecular mass cut-off
440	6 000 dalton
441	6 000 dalton
442	6 000 dalton
570	12 000 dalton
571	12 000 dalton
572	6 000 dalton
573	35 000 dalton
719	60 000 dalton

4.3.1 TUBULAR UF MEMBRANES

4.3.1.1 Test conditions

Linear velocity	2 m/s
Pressure	400 kPa
Feed temperature	25 °C
Feed	Sasol CWBD
pH:	6,5 - 7,6

4.3.1.2 Membranes tested at 0% recovery

Tubular IPS UF membranes, codes 570, 571 and M719 were tested in-house on SASOL effluent at 0% recovery. After approximately 150 h operating time, the flux stabilized at 25 lmh (Fig. 4.2). After a 0,2% Biotex wash for 1 h the initial flux of 30 lmh was re-established, but within 50 h of operation on fresh effluent, the flux returned to 25 lmh.

Although no conductivity retention was expected, a retention between 2 and 7% was achieved (Fig. 4.2). An explanation for this could be the formation of a gel-layer on the membrane surface which offered resistance to transport of multivalent ions.

Analysis of the permeate from the above-mentioned membranes showed that Ca^{2+} and Fe^{3+} were the retained cations. A slight reduction in COD was also detected (Table 4.3).

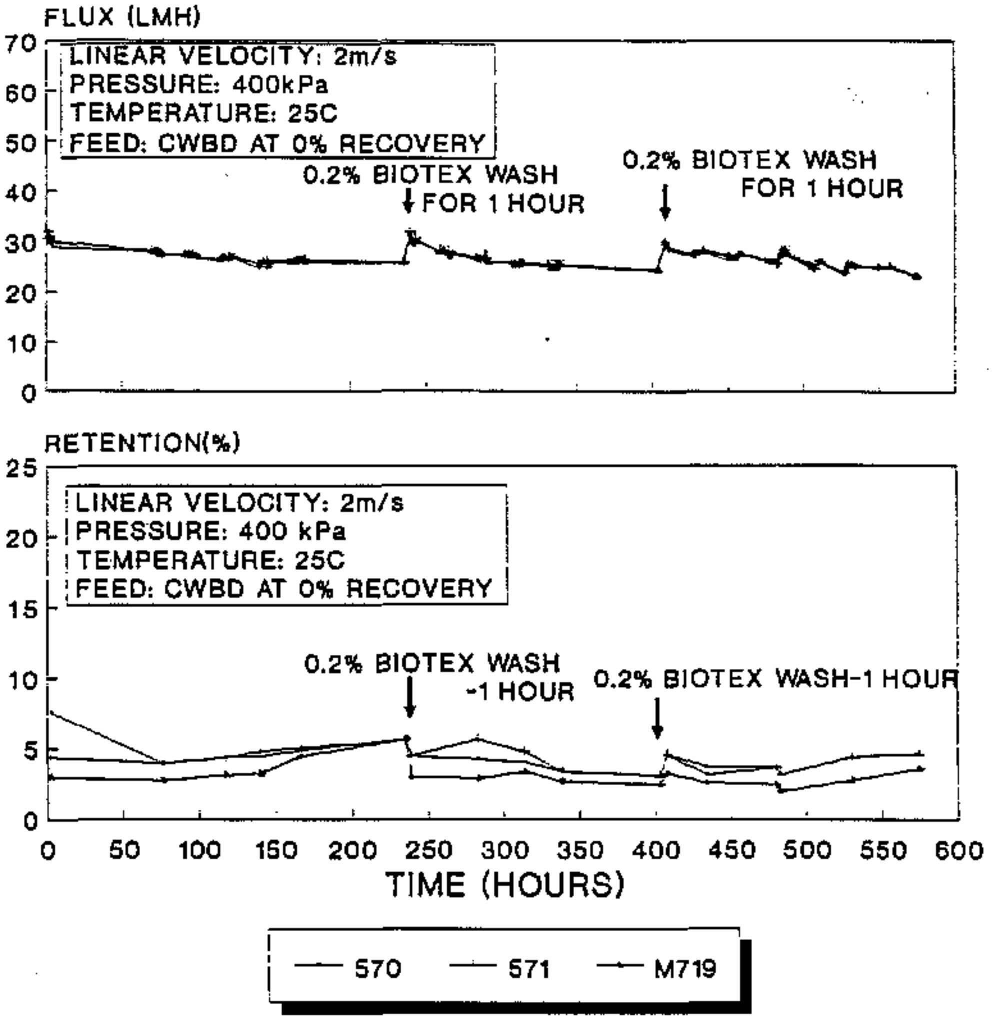


Fig. 4.2:
Flux and retention performances of tubular UF membranes operated on CWBD at 0% recovery.

Table 4.3: Analysis of feedwater and permeates of different UF membranes operated on CWBD at 0% recovery

	Cl^-	F^-	Na^+	SiO_2	Fe^{3+}	COD	Ca^{2+}	Turbidity
Feed water	490	530	723,8	160	9,6	2 650	20,7	59
After UF treatment with membranes listed, operated at 20% recovery.								
719	481	520	720	145	2,9	2 080	5,9	3
570T	485	510	717,5	160	1,5	2 100	5,1	1
571T	488	520	695,2	150	1,8	2 250	4,5	2

4.3.1.3 Membranes tested at 20 - 43% recovery

IPS UF membranes 573, 572, M719, M442, M441 and M440 were tested on SASOL cooling-water blowdown at a product recovery of between 20% and 43%. The initial flux of the different membranes varied between 35 and 55 lmh. Within 200 h the flux of all the membranes stabilized at approximately 25 lmh with a corresponding conductivity retention between 5 and 13% (Fig. 4.3). Membranes of the 719-range stabilized at higher flux-values (30 lmh) with a corresponding salt retention of about 7%. No permanent fouling occurred during the operation, and after every soap wash a dramatic flux increase was evident. This fact was confirmed when the membranes were inspected after 1 000 h of operation.

As in the previous case the membranes were cleaned with an 0,2% Biotex wash every 250 h. After every wash the flux increased dramatically with conductivity retention remaining virtually constant. The fact that the flux was restored to normal levels after every wash showed that no permanent fouling occurred during the operation. This fact was confirmed when the membranes were inspected after 1 000 h of operation and were found to be clean and shiny (i.e. after washes).

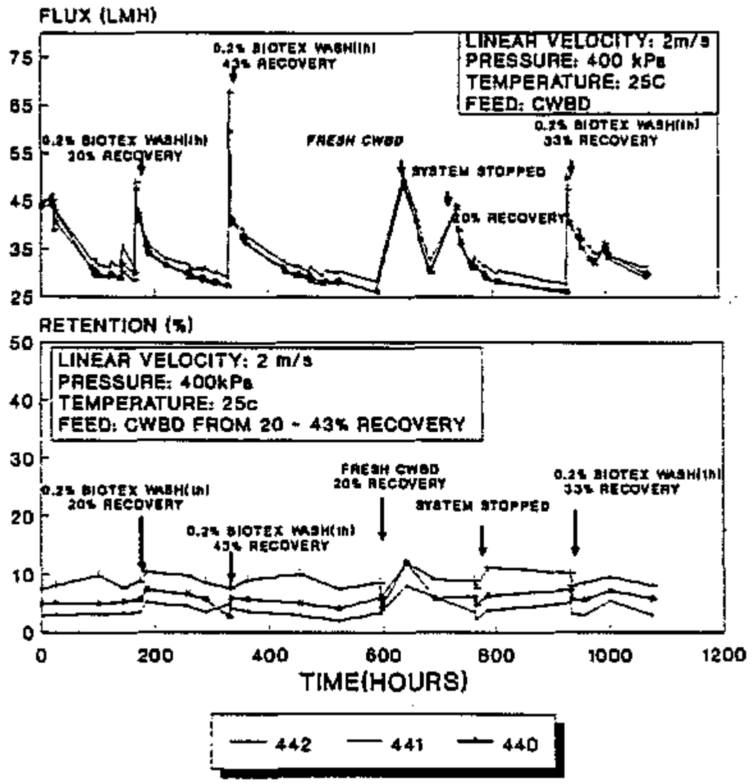


Fig. 4.3:
Flux and retention performances of six sets of different tubular UF membranes operated on CWBD at 20 - 43% recovery.

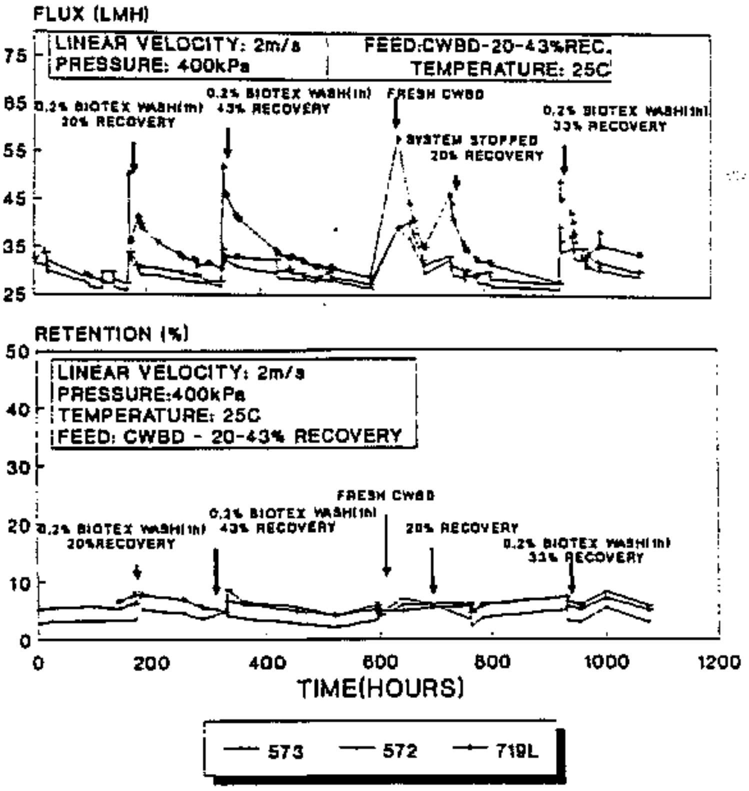


Fig. 4.3: (continued)
Flux and retention performances of six sets of different tubular UF membranes operated on CWBD at 20 - 43% recovery.

Table 4.4: Contents of feedwater and permeates (mg/l) of different UF membranes operated on CWBD at 20% recovery

	Cl^-	F^-	Na^+	SiO_2	Fe^{3+}	COD	Ca^{2+}	Turbidity
Feed water	562	565	990,4	160	10	3 100	25,2	59
After UF treatment with membranes listed, operated at 20% recovery.								
719	530	560	742,8	155	2,2	1 900	4,5	3
440	562	560	780	150	1,5	2 500	5,8	0
441	534	560	828,5	150	1,0	1 800	6,4	1
442	557	563	752,3	160	0,9	1 850	5,1	0
572T	544	560	717,2	155	2,7	2 550	4,5	1
573T	534	550	767	160	1,4	2 600	7,1	2

Analysis of the CWBD feedwater and UF permeates at 20% recovery showed that up to 75% Ca^{2+} and 50% Fe^{3+} were removed (see Table 4.4). Slight COD retentions also occurred, although it varied from one membrane to another and there was almost 100% colour removal. Cl^-, F^-, Na^+ and SiO_2 levels remained virtually the same.

Although higher retentions with the lower MM cut-off membranes were evident, it appeared that the overriding factor influencing salt retention could have been the presence of a gel-layer being established during operation.

4.3.1.4 Flocculants used in conjunction with UF membranes

It was decided to use a range of flocculants in conjunction with UF membranes to:

(i) determine whether it was possible to establish a dynamic gel-layer (using the flocculant) on the membrane in order to increase salt retention during the UF stage and thus lessen the burden on the salt removal stage; and

(ii) determine whether an increase in permeate flux would occur because suspended solids would be flocculated and thus offer less resistance to mass transfer.

Flocculants Zetag 57, Magnafloc LT31 and Magnafloc 1597 (Chemserve) were used in conjunction with the available UF membranes. Disappointing results were obtained. Severe fouling of the membranes occurred in the case of Zetag 57 and the remaining two flocculants had no effect on either the flux or retention properties of the membrane.

4.3.1.5 Effect of pH on membrane performance

It was found that an increase in pH resulted in a significant increase in flux (up to 50 lmh in the case of UF membrane 719) and a slight drop in conductivity retention (refer Fig. 4.4). However, due to the pH sensitivity of the membrane substrate material, the life span of these membranes decreases dramatically when operated at pH levels above 10.

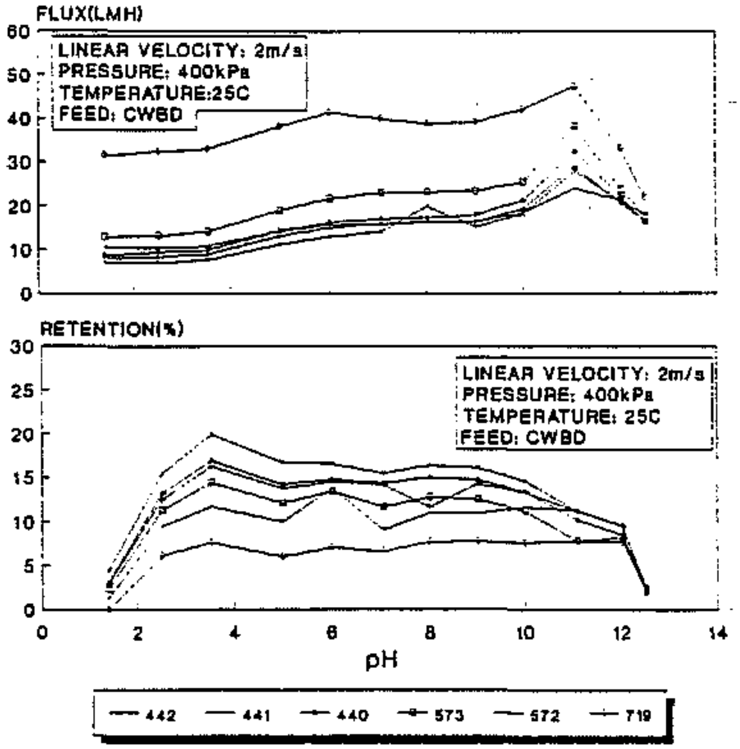


Fig. 4.4:
Performances of different tubular UF membranes showing the effect of pH on flux and retention.

4.3.2 CAPILLARY UF MEMBRANES

Tests conducted by Sasol in the past suggested that the suspendid solids and macromolecules present in the effluent inhibit crystal growth and subsequent scale formation on equipment. For this reason it can be argued that by removing suspended solids and macromolecules, an increase in scale formation (e.g. heat exchangers) can be expected. For this reason it is important to remove suspended solids as well as scale-forming salts. Salts could be removed by RO or ion-exchange.

Although various problems could be foreseen with regard to using a capillary UF membrane system, the possible advantages of such a membrane treatment system were very attractive. It was therefore decided to test and evaluate an experimental capillary UF membrane developed at IPS.

The advantages of capillary membranes are:

(i) relatively high surface to packing density ratio;

(ii) self-supporting;

(iii) high drag-force-to-pump energy ratios when compared with that of tubular membranes;

(iv) low module cost; and

(v) low operating pressures and subsequent low running costs.

4.3.2.1 Test conditions

Linear velocity	0,25 m/s
Pressure	200 kPa
Feed temperature	25 °C
Feed	Sasol CWBD
pH	6,5 - 7,6

4.3.2.2 Test results

As shown in Figure 4.5, the flux of the capillary membrane module stabilized at 10 lmh with a corresponding conductivity retention of 5%. One of the reasons for the relatively poor flux was the blockage of the capillary entrances at the end of the module by suspended solids. If a capillary end blocks, no linear flow through the membrane exists to scour that membrane surface. It acts as an dead-end filter and a clogging cake layer forms. Another disadvantage of the capillary membrane system was that it could not be cleaned by mechanical means (e.g. sponge-ball cleaning). This problem can, however, be overcome by applying suitable washes, for example, enzymatic detergent washes and backwashing.

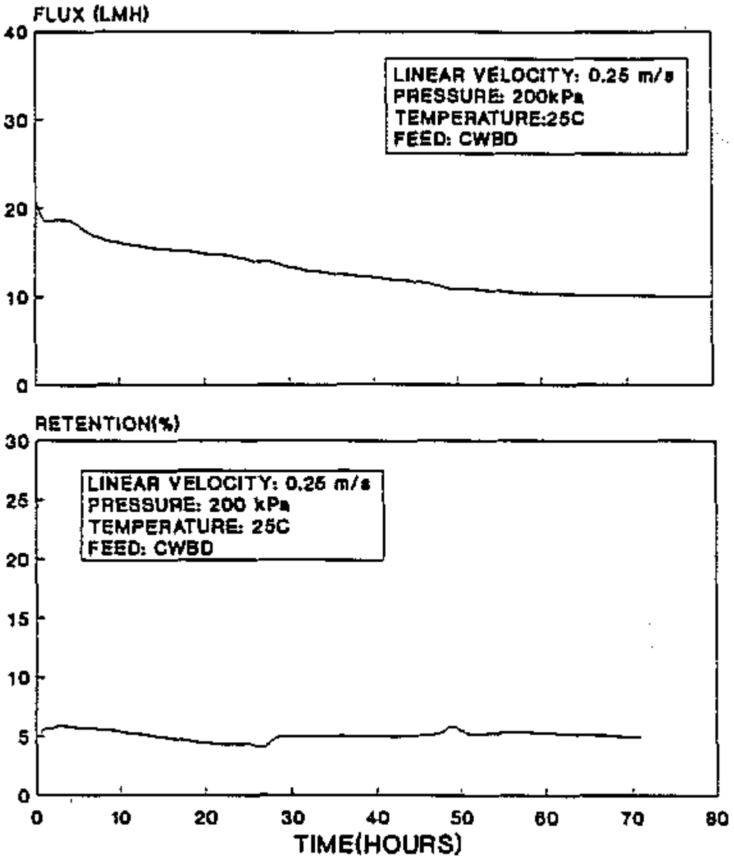


Fig. 4.5:
Flux and retention performances of capillary UF membranes operated on CWBD.

4.3.3 TUBULAR NANOFILTRATION MEMBRANES

4.3.3.1 Properties

A robust PVOH NF membrane was recently developed at IPS [Ref 4.2]. This membrane system offered the following advantages:

(i) dry storage (i.e. wet-dry cycling);

(ii) wide operating pH range;

(iii) not easily chemically oxidized; and

(iv) robustness.

These membranes exhibited typical NF performances of: 40% and 80 lmh (1 000 ppm NaCl solution) and 85,9% and 35 lmh (1 000 ppm $MgSO_4$ solution). These tests were conducted at 2 MPa, 25 °C and a linear flow velocity of 1,5 m/s.

This experimental membrane was tested for robustness (molecular abbrasion resistance) by subjecting it to extensive testing on an oversaturated $CaSO_4$ slurry. The feed consisted of 10 000 ppm $CaSO_4$ slurry and, since the solubility of $CaSO_4$ is approximately 2,8 g/l, the feed contained approximately 7,2 g/l undissolved solids.

4.3.3.2 Membrane performance

A. $CaSO_4$ slurry test

Test Conditions

Feedwater	10 000 ppm $CaSO_4$ slurry
Temperature	25 °C
Pressure	2 MPa
Linear velocity	2 m/s

Test Results

Figure 4.6 shows the $CaSO_4$ permeate flux and retention values versus operating time. It was evident that the retention decreased slightly and then reached a limiting value of approximately 60%. The flux values varied slightly between 35 and 37 lmh.

This test showed that the PVOH NF membranes (crosslinked with $K_2S_2O_8$) were resistant to abrasion by slurry feeds for at least 25 days. It should also be noted that the membranes in this test had been subjected to rigorous ageing treatment beforehand. New membranes of this type were expected to give much higher $CaSO_4$ retentions (of the order of 80%).

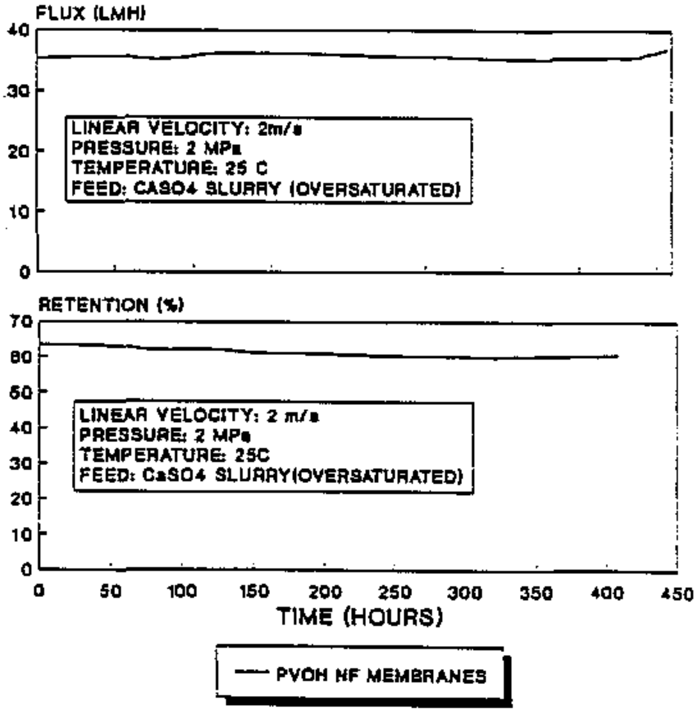


Fig. 4.6:
Flux and retention performances of PVOH NF membranes operated on an oversaturated $CaSO_4$ slurry.

B. Tests on CWBD effluent

Test Conditions

Linear velocity	2 m/s
Pressure	2 MPa
Temperature	25 °C
Feed	CWBD (0% recovery)

Test Results

Two sets of experimental membranes were tested on the effluent. Good results were obtained with regard to flux and retention (Fig. 4.7). Stabilized fluxes varied between 15 and 25 lmh with corresponding conductivity retentions of 40 to 75%. Analysis of the permeate showed that 99% of all organic substances had been removed, indicating that a major percentage of the conductivity retention could be regarded as organic retention. These results were typical of a NF membrane. Each membrane tested was manufactured under different conditions and according to a different formulation and therefore differences in membrane performance will be evident in the test results. Only the best performing membranes were considered for further development and evaluation.

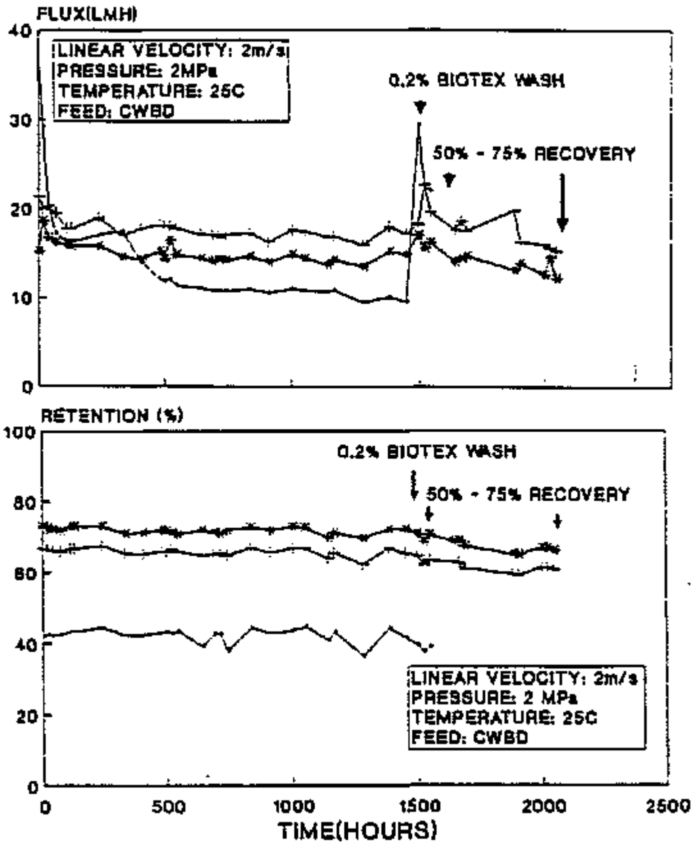


Fig. 4.7:
Flux and retention performances of six different PVOH NF membranes operated on CWBD (0% recovery).

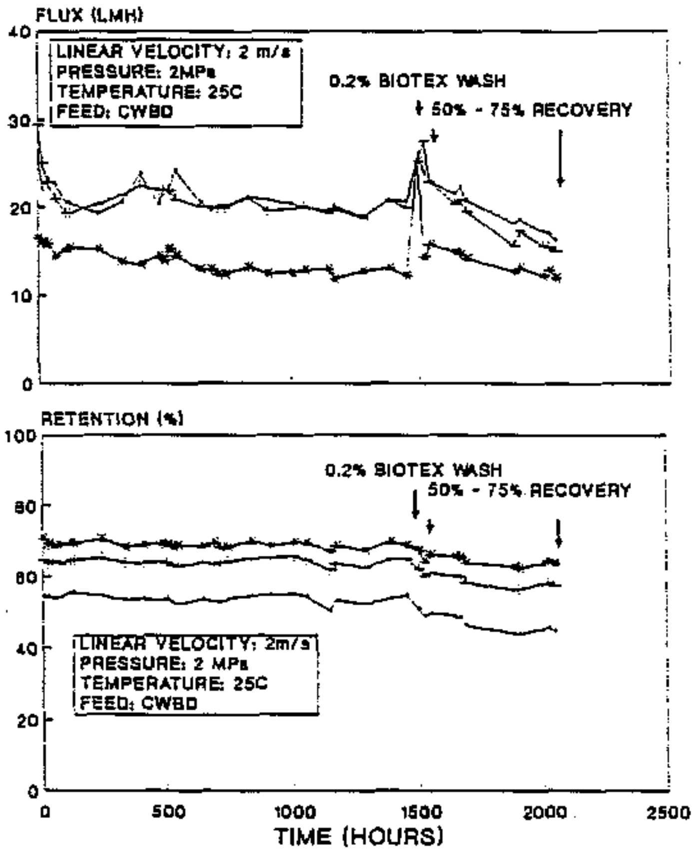


Fig. 4.7: (continued)
Flux and retention performances of six different PVOH NF membranes operated on CWBD (0% recovery).

4.4 ON-SITE MEMBRANE EVALUATION

4.4.1 BACKGROUND

After the satisfactory completion of laboratory-scale membrane evaluation studies at IPS, three test-rigs were installed at Secunda:

(i) a capillary UF membrane test rig;

(ii) a tubular UF membrane test rig; and

(iii) a tubular RO membrane test rig.

The following two approaches were to be investigated: i) UF as pretreatment to RO and ii) direct application of RO and NF.

Many various experimental tubular UF, capillary UF, NF and RO membranes were to be tested on fresh Sasol industrial effluent. The membranes were to be tested at increasing concentrations (% recovery) to determine to what extent these concentrations influenced the performance of the membranes.

4.4.2 TEST RESULTS

4.4.2.1 Tubular ultrafiltration membranes

A. Batch 1

An experimental batch of low MMCO PS UF membranes was installed in the UF test-rig at Secunda. The following experimental tubular UF membranes were tested: E578T/744, E577/743, 442, 440 and the commercial UF membrane M719L (originally researched an developed at IPS). The membranes had the following PEG MMCOs:

E578T/744	80 000 dalton
E577/743	60 000 dalton
442	6 000 dalton
440	6 000 dalton
M719L	60 000 dalton

Results of the evaluations of the membranes are given in Figure 4.8. The test was performed at 0% recovery.

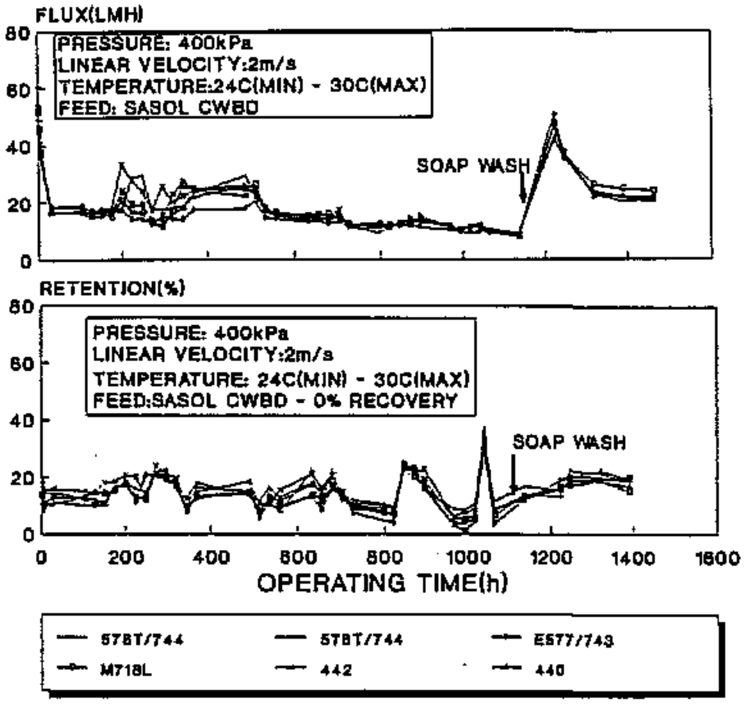


Fig. 4.8:
Flux and retention performances of six sets of different tubular UF membranes operated on CWBD at 0% recovery.

B. Batch 2

Further experimental PS UF tubular membranes, with different MMCOs, (codes: 440, 442, 572, 573 and 574), were installed and tested, using the commercial M719L UF membrane as control. The PEG MMCOs for the further experimental membranes were:

440	6 000 dalton
442	6 000 dalton
572	6 000 dalton
573	35 000 dalton
574	25 000 dalton

Results of a pure-water flux test are given in Figure 4.9. A test run of 75 h on CWBD at 0% recovery was then carried out, followed by a range of tests at different concentrations (recoveries) (a 0,2% soap wash preceded each test). This was done to determine the effects of different concentrations of effluent on flux and retention, without taking the effect of fouling into account. Results are given in Figure 4.10.

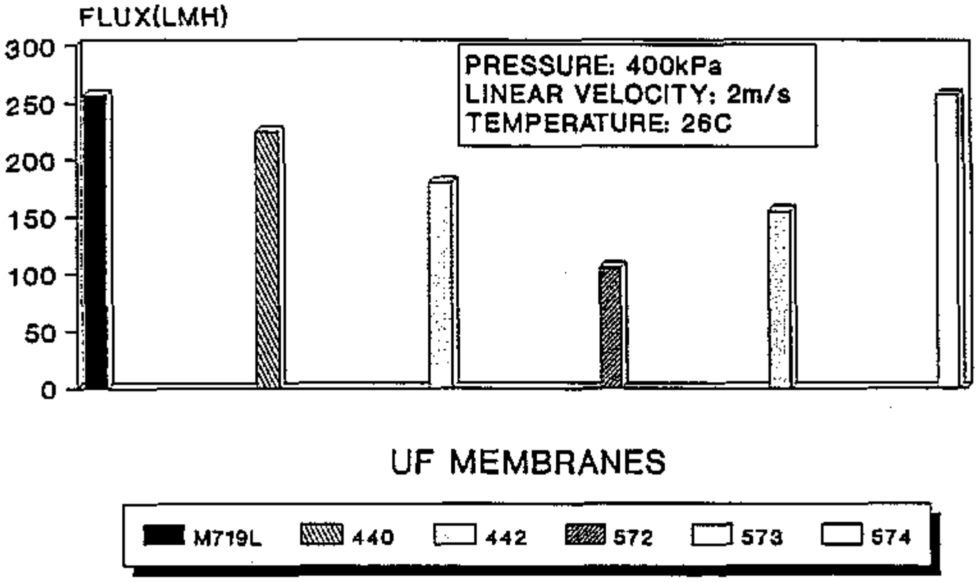


Fig. 4.9:
Pure-water flux - Tubular UF membranes.

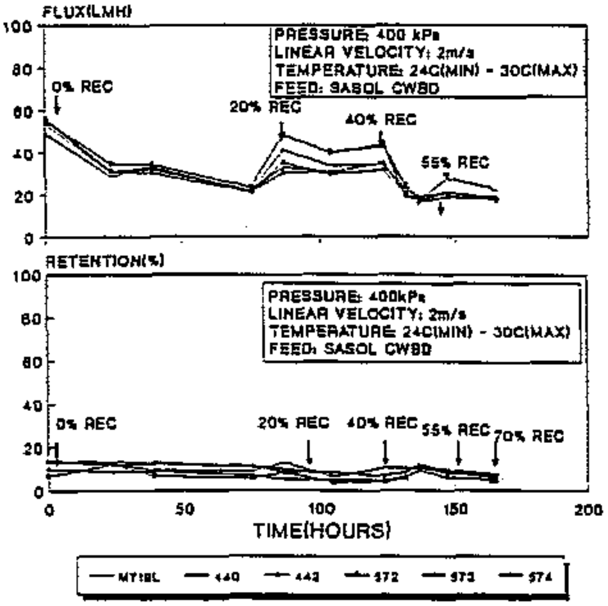


Fig. 4.10:
Flux and retention performances of six sets of different tubular UF membranes operated on CWBD at different recoveries.

Figure 4.11 shows a marked decrease in flux with an increase in feed concentration. A slight reduction in retention is also observed in the plot of retention against percentage recovery.

Analysis of the UF permeates showed, surprisingly, a reduction of 20% $CaSO_4$ (average for all UF membranes tested). The colour retention was 99% and the COD retention varied between 20% and 25%. The reductions in COD and $CaSO_4$ concentrations were most probably due to gel-layer formation on the membrane surface.

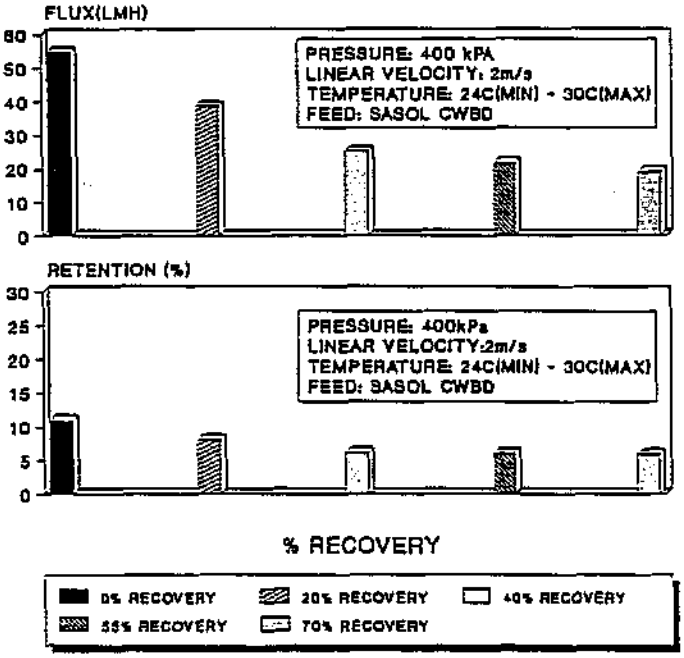


Fig. 4.11:
Flux and retention performances of different tubular UF membranes, plotted against different concentrations (recoveries) of CWBD.

The design of the tubular UF membrane test rig is shown in Figure 4.12.

Assumptions made were the following:

Maximum back pressure required:	500 kPa
Maximum linear velocity required through tubular membranes:	2 m/s
Diameter of tubing used:	12,7 mm

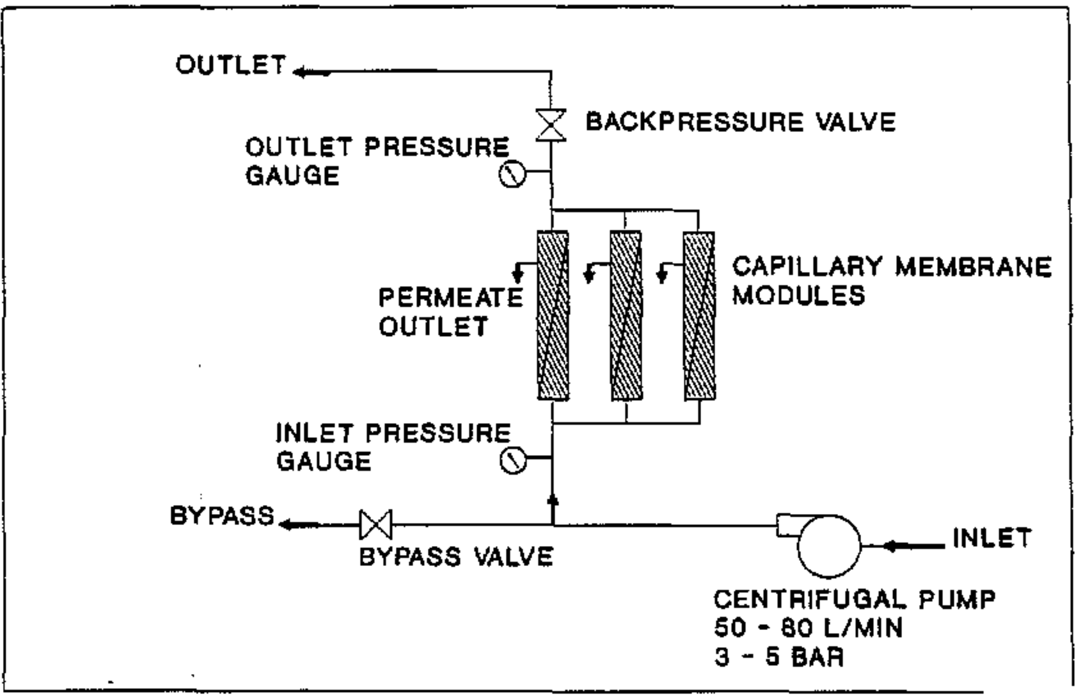


Fig. 4.12:
Tubular UF membrane test-rig design.

4.4.2.2 Capillary ultrafiltration membranes

Two experimental capillary PS UF modules were tested on the effluent. The advantages of these membranes are their higher packing density (when compared with tubular membranes) and their usefulness at lower operating pressure (200 kPa). Problems were, however, expected with regard to blockage and bridging at the module entrance. Membranes can become blocked by particles larger than, or of the same size as, the capillary membrane entrance (approximately 1 mm), which prevent normal fluid-flow. This could, however, be prevented by using a micron-sized filter ahead of the capillary membrane operation. Bridging is a term which describes the build-up, with time, of very fine suspended solids at the capillary membrane entrance. This phenomenon is difficult to combat and limits the use of these systems in certain applications. (The answer most probably lies in the use of different manifolding systems to prevent solids build-up.)

After 200 h of operation, the membrane flux stabilized at 10 lmh . The reduction in flux after 200 h was due to bridging which was very clear upon inspection of membranes during and after the test (Fig. 4.13). Varying retentions can be ascribed to variations in effluent composition.

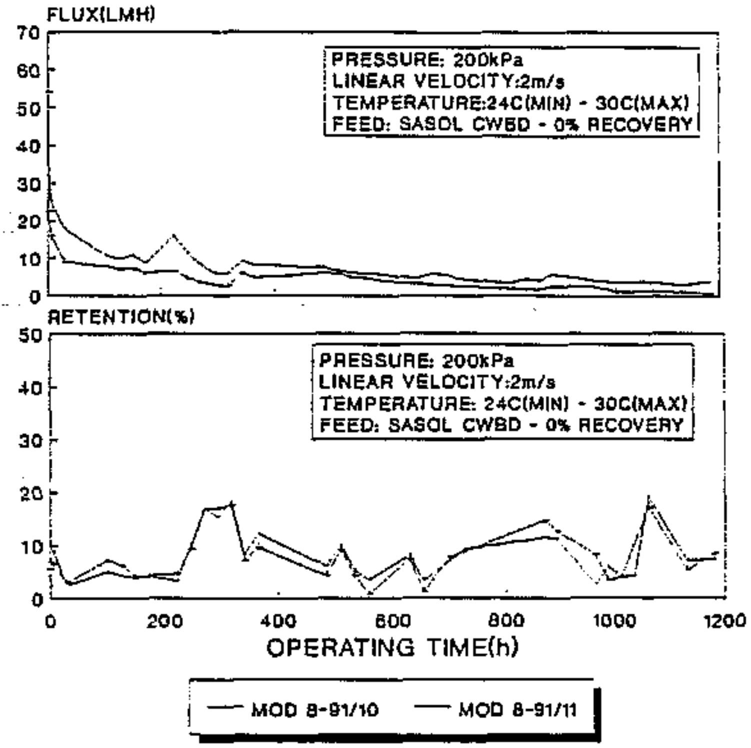


Fig. 4.13:
Flux and retention performances of capillary UF membranes operated on CWBD.

The design of the capillary membrane test-rig is shown in Figure 4.14.

Assumptions made were the following:

Number of capillary membranes per module:	200
Average capillary membrane ID:	1,4 mm

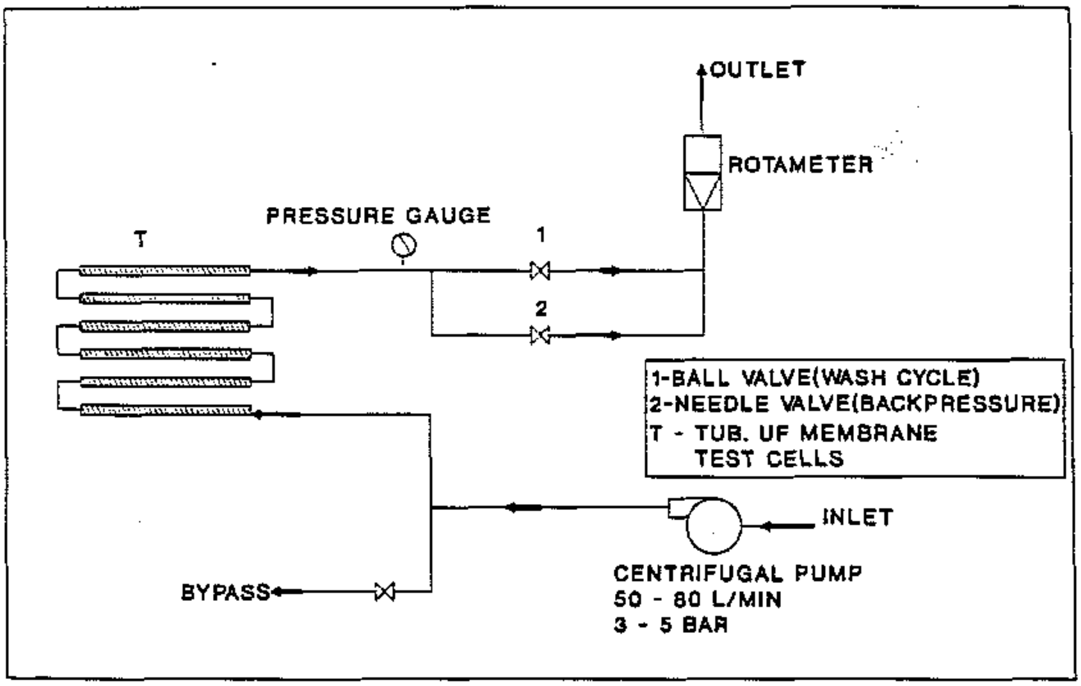


Fig. 4.14:
Capillary membrane test-rig design.

4.4.2.3 Tubular nanofiltration and RO membranes

A. Nanofiltration membranes

Various experimental PVOH NF membranes were installed and tested at 2 MPa directly on CWBD effluent (Fig. 4.15). A conventional CA RO membrane was included as control in the experiment. One advantage of the PVOH membranes was that dry storage was posssible: a system could be shut down for long periods of time without damage being caused to the membranes. A further advantage of the NF membranes was that higher average flux-values than those of conventional CA membranes should be attained, requiring lower operating pressures.

Although the general conductivity retention of the PVOH NF membranes was, on average, 75% compared to the 99% retention of the CA membranes, analysis of the permeate (Figs. 4.16 to 4.22) showed that the SO_4^{2-} and PO_4^{3-} retention-values were comparable to those of CA membranes (99,9% retention). Removal of $CaSO_4$ and phosphates is important in view of their scale-forming potentials.

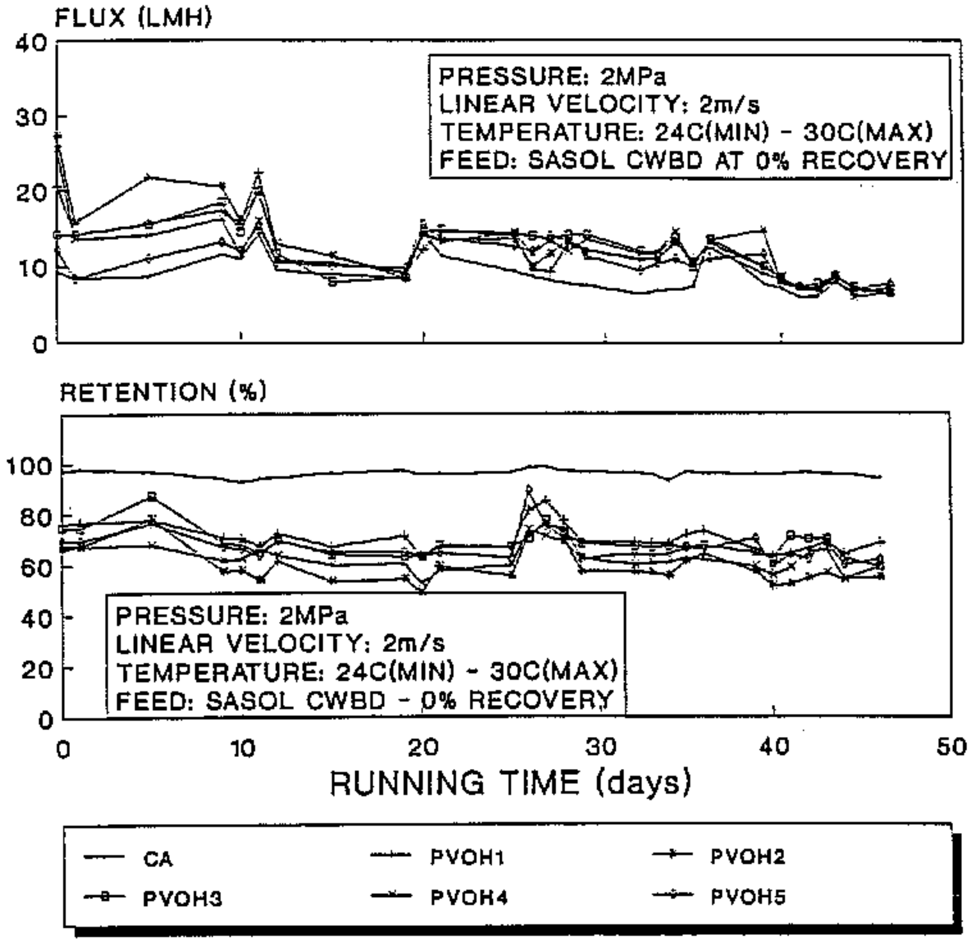


Fig. 4.15:
Flux and retention performances of different PVOH NF membranes operated on CWBD.

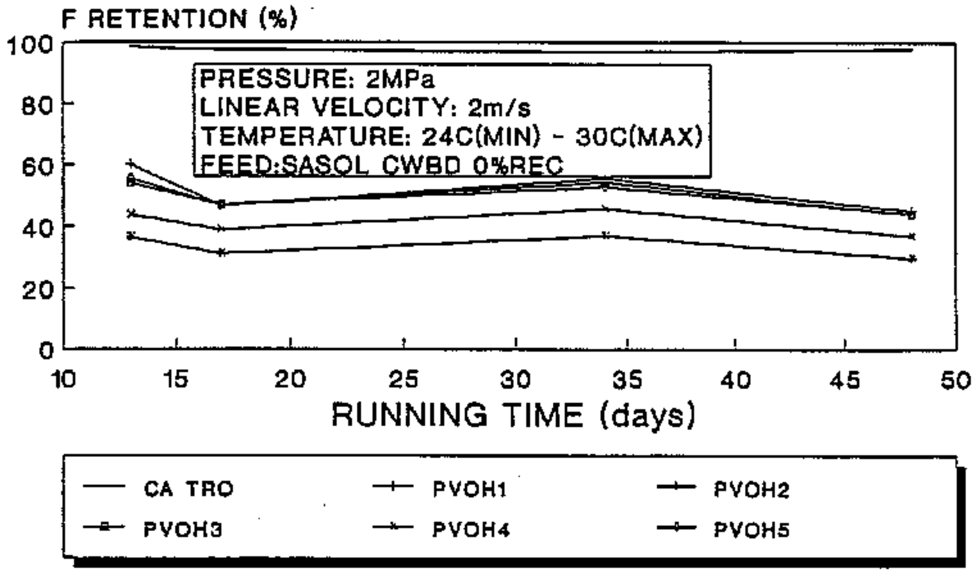


Fig. 4.16:
Fluorine retention of PVOH NF membranes.

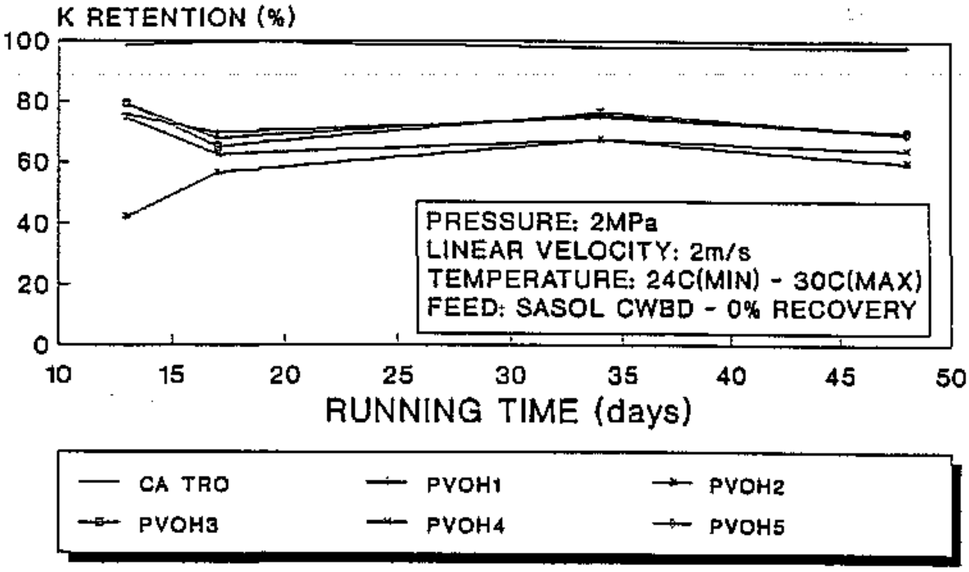


Fig. 4.17:
Potassium retention of PVOH NF membranes.

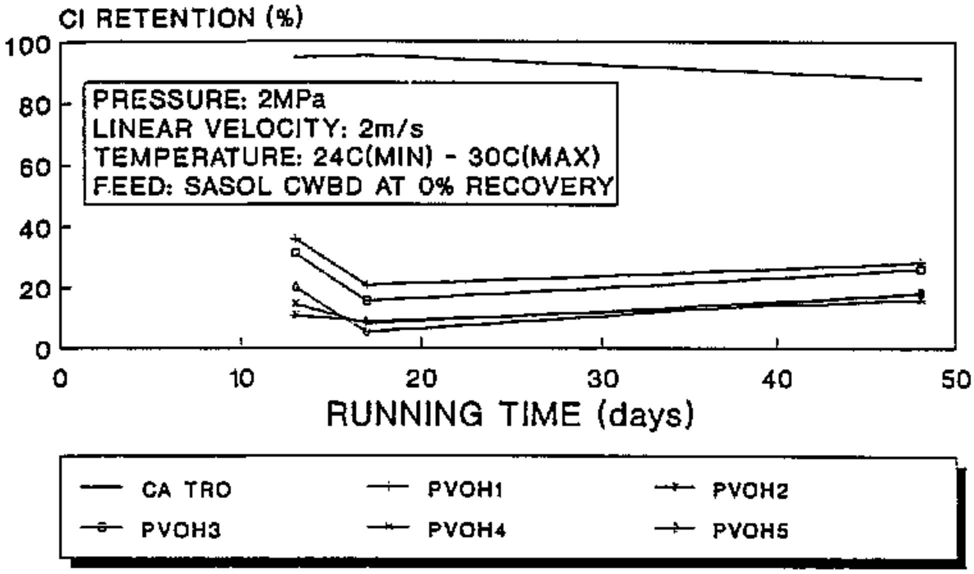


Fig. 4.18:
Chloride retention of PVOH NF membranes.

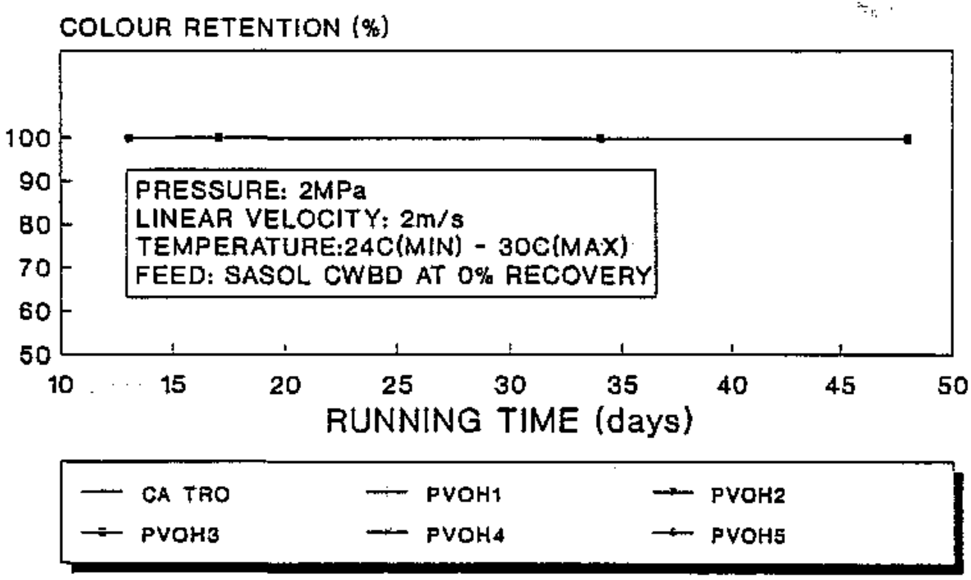


Fig. 4.19:
Colour retention of NF membranes.

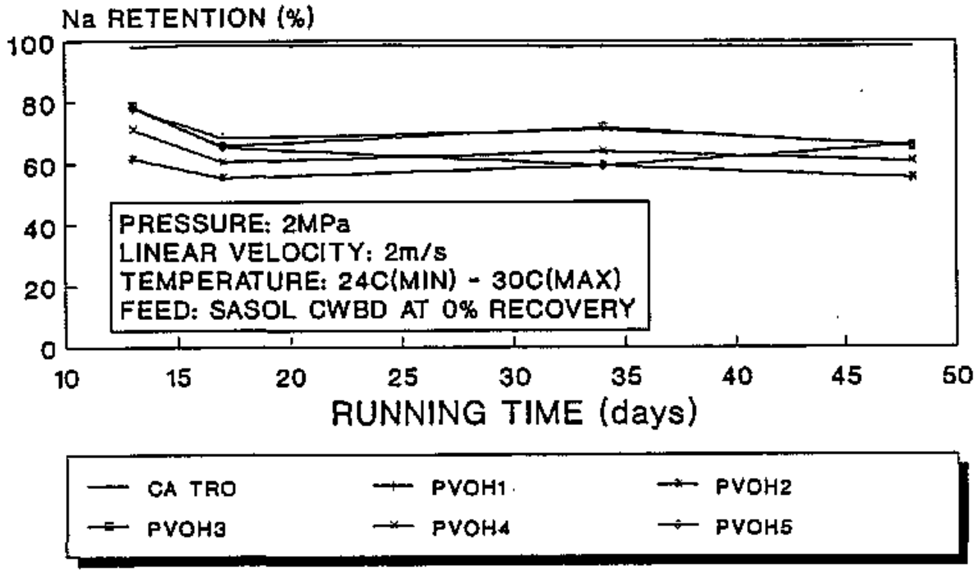


Fig. 4.20:
Sodium retention of NF membranes.

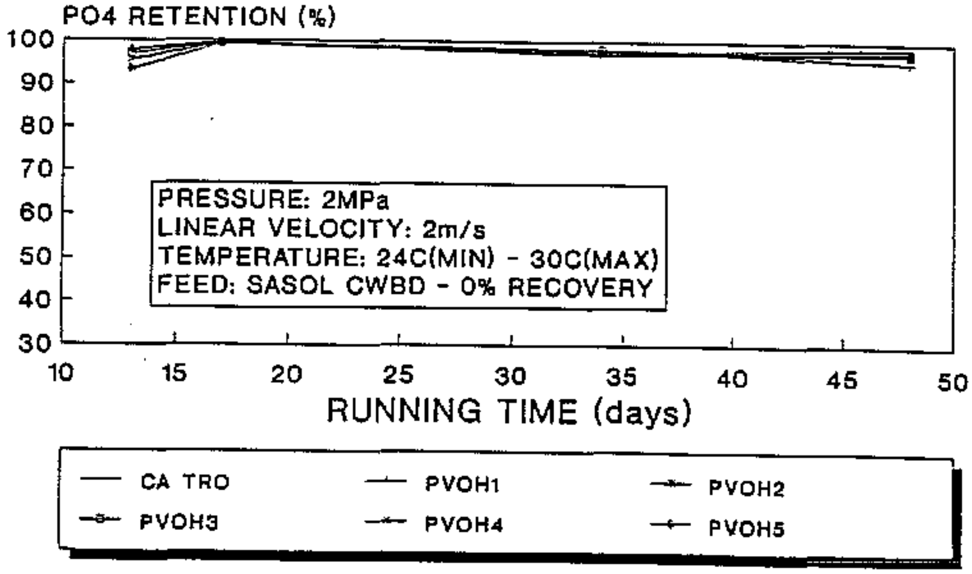


Fig. 4.21:
Phosphate retention of NF membranes.

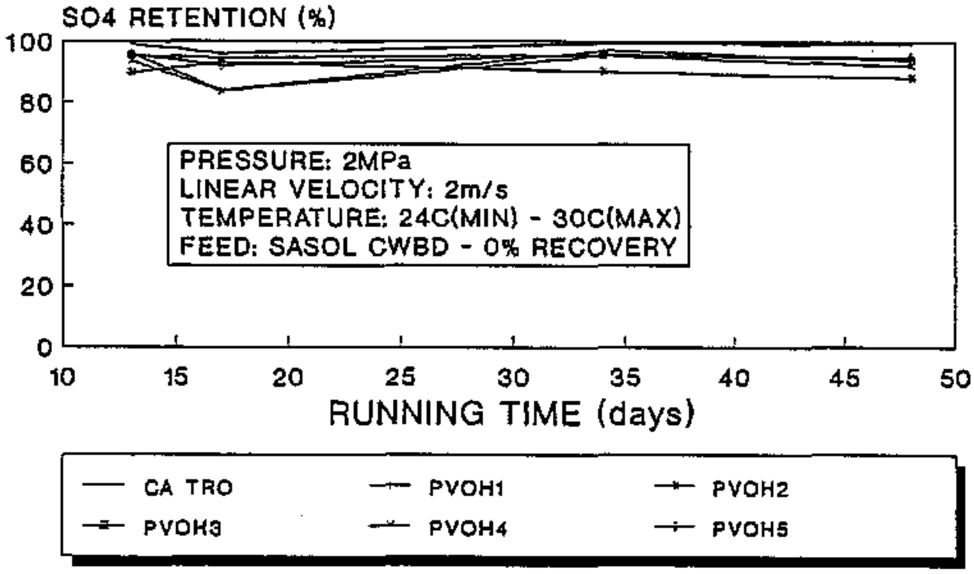


Fig. 4.22:
Sulphate retention of NF membranes.

B. Modified PVOH RO membranes

Experimental ultra-thin-film modified composite PVOH RO membranes were also tested at Secunda to determine their performance on CWBD effluent. Three different types of these membranes (codes: HOIPS, CAMOH and CAMPIP, described in section 3.3) were tested. After laboratory tests with a 2 000 ppm NaCl solution, retentions of above 94% were obtained; the CAMPIP membrane had a corresponding flux of 60 lmh at 2 MPa.

The effluent was concentrated to give an eventual recovery of 75%. The result was an expected reduction in flux to about 10 lmh. The CAMPIP membrane gave the best results for both flux and retention (Fig. 4.23). The membranes were tested at a relatively low operating pressure of 2 MPa.

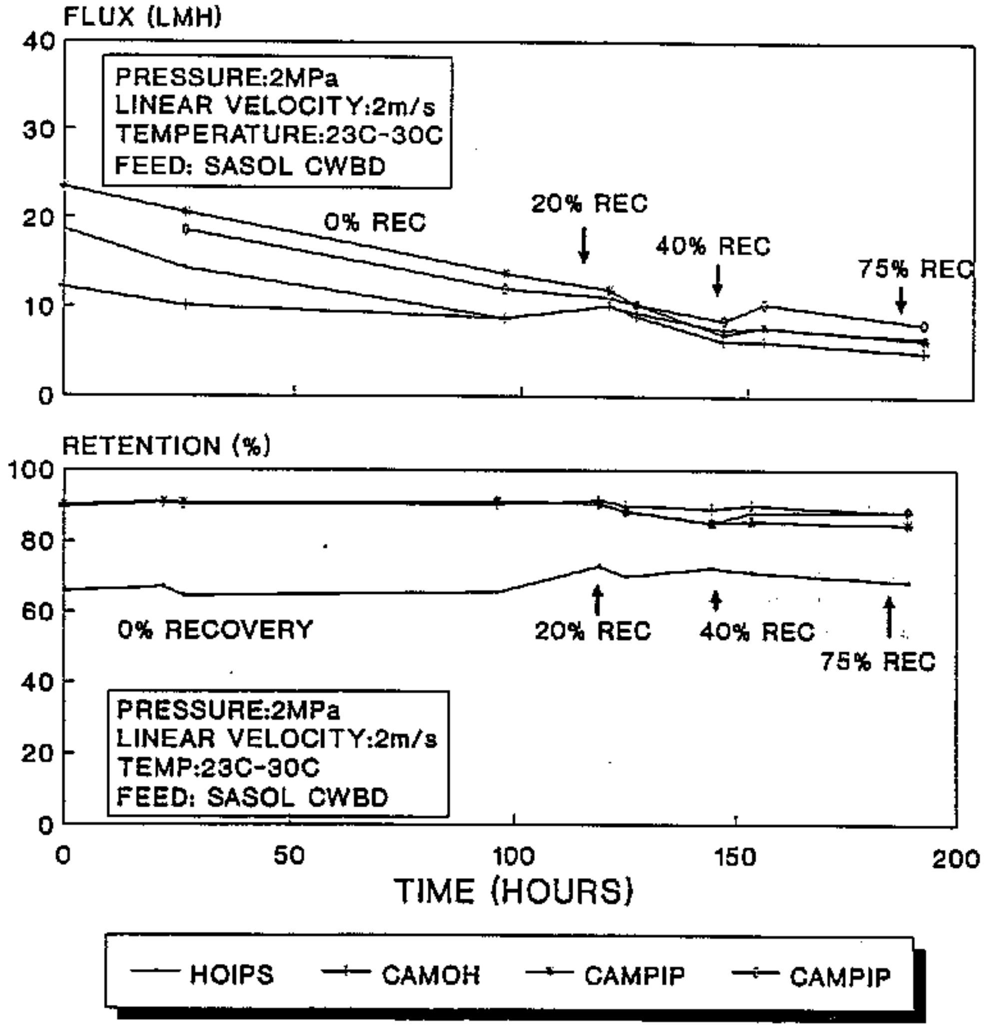


Fig. 4.23:
Flux and retention performances of different modified PVOH RO membranes operated on CWBD at different recoveries.

PVOH RO membranes were tested on a test-rig, designed as shown in Figure 4.24.

An existing RO test-rig unit with a positive displacement pump included was modified to suit requirements. (A maximum backpressure of 4 MPa with corresponding volumetric flowrate of approximately 1 000 l/h was required.)

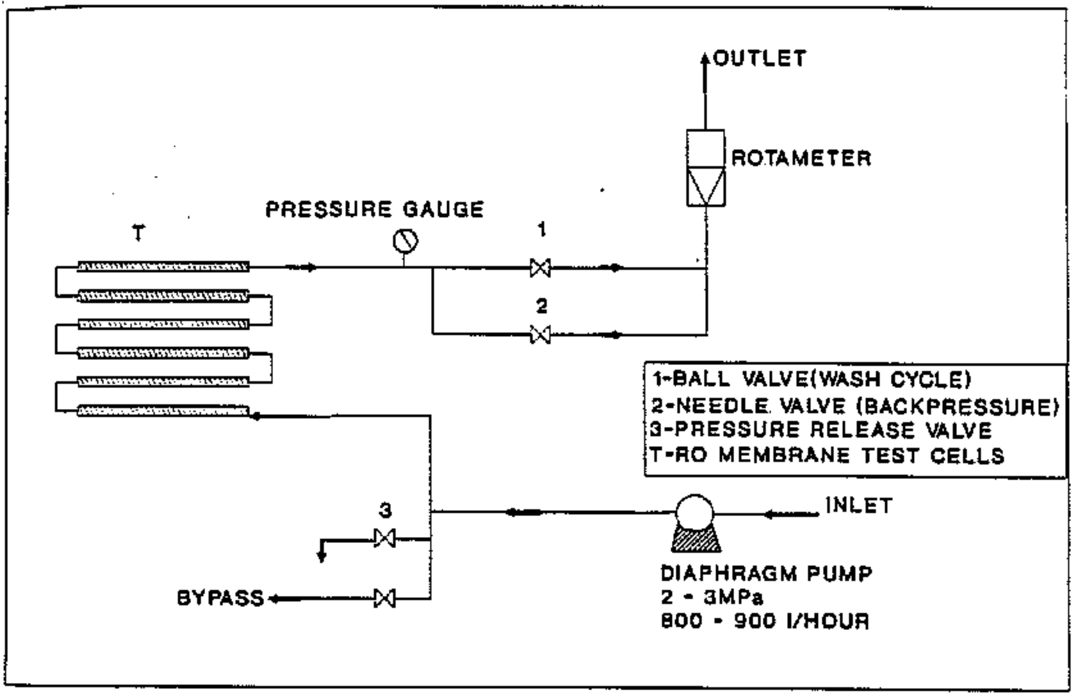


Fig. 4.24:
Tubular RO membrane test-rig design.

4.5 DISCUSSION

UF and RO membranes tested in this study proved, with the exception of a few, to be chemically stable after being exposed to an effluent with a major fouling potential and which contained a variety of dissolved and suspended solids. It was found with UF membranes, in particular, that a soap wash after a period of operation always resulted in restoration of the original fluxes. Suspended solids and macromolecules could be effectively removed by UF and the salt concentrations were greatly reduced by RO.

4.5.1 ULTRAFILTRATION

A good quality permeate with 100% removal of suspended solids and close to 100% of colour was achieved by UF. This would result in a drastic increase in RO flux when UF is used as pretreatment method. A cost study will have to be done to determine whether this operation is a viable one, in view of rapid fouling of the UF membranes and the need for subsequent frequent washing to maintain higher average fluxes. It was interesting to note that 50% to 70% of Fe^{3+} and SO_4^{2-} were removed because of the creation of a gel-polarized layer on the UF membrane surface. The retention of sulphates should reduce scale formation to a large extent.

4.5.2 NANOFILTRATION

In the case of NF, the biggest problem proved to be the relative rapid, although not permanent, fouling of the membranes. The reason for this was probably the phenomenon of gel-polarization. A general conductivity retention of approximately 70% and 99% PO_4^{3-}, SO_4^{2-} and colour retention were achieved in the case of NF. Although higher initial average fluxes were achieved by NF, compared to RO, the flux evened out at more or less the same level as that achieved by RO (after approximately 50 h of operation).

4.5.3 REVERSE OSMOSIS

RO showed 95% to 99% conductivity retention, while individual retentions of Na^+, colour, F^-, PO_4^{3-}, K^+, SO_4^{2-} and Cl^- were never lower than 90%. Again, the main problem seemed to be rapid fouling of the membranes. Although fouling was not permanent, the need for frequent soap washes during operation would probably make direct application of RO a less attractive operation.

With frequent soap washes or with the help of mechanical cleaning methods such as sponge-ball cleaning, an average flux of 25 to 30 lmh (with a corresponding average retention of 95%) should be achieved with a RO system operated at 4 MPa. When a mass balance calculation is made over a typical RO unit consisting of a hypothetical number of 660 x 2,4 m modules (equivalent to 1 000 m² membrane area) (Fig. 4.25), the water recovery was found to be 25%. In this case the total maximum CWBD stream of 2 700 m³/d (equivalent of 112 500 kg/h) was used as feedstream. In practice, RO treatment of a smaller sidestream would probably be more practical. The power costs incurred could be estimated by calculating the plant productivity [Ref. 4.2] as follows:

Plant productivity = Mass TDS and SS removed/MJ energy expended

Where:

Mass TDS, SS removed = Permeate flow x (Feed TDS, SS - Permeate TDS, SS)

Power cost incurred = Feed pressure x Feed flow rate

From the above formulas the productivity of a RO plant, as stipulated in the mass balance (Fig. 4.25), could be calculated and was found to be 0,465 kg/MJ energy expended.

A possibility for RO operation could be the ETP (excess to ponds) bleedstream. The concentrated portion could then be transported to the evaporation ponds or used for ash conditioning.

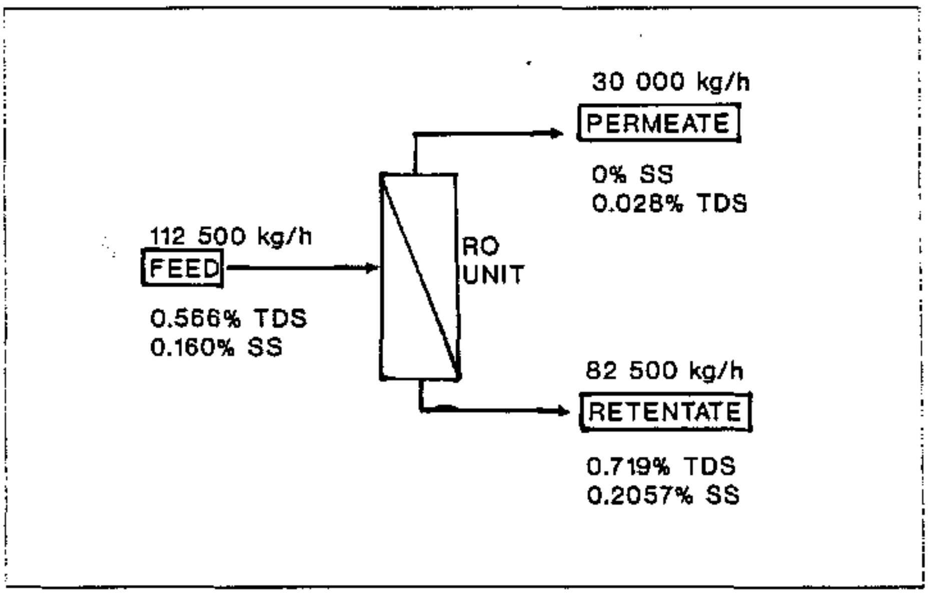


Fig. 4.25:
Mass balance across a typical RO unit.

4.6 CONCLUSIONS

The effluent stream selected for testing of the membranes, namely CWBD, was an extreme case, especially with regards to fouling potential. The opportunity offered by Sasol to IPS was of great value to research on membrane applications. The testing of membranes on site supplied IPS with valuable information regarding membrane performance. Problem areas could also be identified with regard to operating limits.

UF and RO membranes tested in this study proved to be, with the exception of a few, chemically stable after being tested on an effluent with a major fouling potential and which consisted of a variety of dissolved and suspended solids. In particular it was found with UF membranes that a soap wash, after a period of operation always resulted in restoration of the original fluxes. It was found that suspended solids and macromolecules could be removed effectively by UF, while the salt concentrations were greatly reduced by RO.

A good quality permeate with removal of 100% suspended solids and close to 100% colour was achieved by UF. The use of UF as a pretreatment method should lead to a drastic increase in RO flux. (A cost study will have to be done to determine whether this operation is a viable one, in view of rapid fouling of the UF membranes and the need for subsequent frequent washing to achieve higher average fluxes.)

A general conductivity retention of approximately 70% and 99% PO_4^{3-}, SO_4^{2-} and colour retention were achieved in the case of NF. The biggest problem appeared to be the relatively rapid, although not permanent, fouling of the membranes.

RO showed 95% to 99% conductivity retention, and individual retentions of Na^+, colour, F^-, PO_4^{3-}, K^+, SO_4^{2-} and Cl^- were never lower than 90%. The membranes fouled rapidly and frequent soap washes were required to restore performance. This would probably make direct application of RO a less attractive operation.

CHAPTER 5

POTASSIUM BITARTRATE REMOVAL FROM WINE RESTS WITH PRESSURE-DRIVEN MEMBRANES

5.1 INTRODUCTION

During the fermentation and stabilization of wine, wine lees are deposited at the bottom of the stabilization tanks. At present the only useful by-product of wine-lees, an otherwise noxious by-product of wine making, is potassium bitartrate (KHT). Potassium bitartrate is an important product since it is used extensively in the food and beverage industry and is expensive to import. Although wine lees contains up to 25% potassium bitartrate, it is of very little value in this state and poses a pollution problem for wine cellars. When isolated, the yeast cells and protein fractions of wine lees (see Appendix A.1) could be valuable by-products as these are sought after products in the food (e.g. yeast extract) and animal feed industries [Refs. 5.1, 5.2, 5.3 and 5.4].

The colloids and macromolecules in wine lees could possibly be separated by UF, and RO could be used to retain KHT.

A number of problems are, however, foreseen:

(i) certain proteins foul membranes rapidly; and

(ii) previous experimental data has shown that a certain fraction of the KHT has an affinity for certain proteins and colloids, making it difficult to remove all the KHT present in the wine lees.

Brennochem currently buys the wine lees as a by-product from wine cellars. The wine lees are therefore transported over large distances to the factory before processing can begin. This transport is in itself very costly and an easier and more compact process would have the advantage that processing units could possibly be installed at wine cellars or at various sites in different wine-producing areas.

At present a chemical process, the hydrocyclone/calcium process, is used to recover the potassium bitartrate. This process has certain disadvantages:

(i) it is inefficient, as large quantities of KHT go untreated through the system and end up with wine rests that are disposed of;

(ii) in the chemical process various points of separation exist, and at each separation a new effluent stream that has to be dealt with in evaporation dams, comes into existence;

(iii) the waste is in a diluted form at the point of disposal and large tankers are used to transport this liquid to disposal areas, which is very costly; and

(iv) the process is not compact enough for plants to be erected at different wine-producing areas.

The new application of membranes to recover potassium bitartrate from wine lees and the possibility of recovering valuable protein and yeast cells by means of membrane fractionation was investigated. Towards these goals the following was considered: To obtain complete separation between high-molecular-mass solutes (proteins and yeast cells) and low-molecular-mass solutes (KHT), the retentate was to be diluted with a solvent (water) so that the low-molecular-mass solutes were washed out. This type of operation is called diafiltration. UF membranes were used in diafiltration mode to "wash" the wine lees slurry, thus separating the potassium bitartrate solution from the yeast cells and proteins. The potassium bitartrate-rich permeate, collected after UF, was then concentrated by means of RO and NF to allow subsequent precipitation of the product.

5.2 OBJECTIVES

The main objective of this study was therefore to determine whether membrane processes could be applied successfully to the fractionation of wine lees to produce useful by-products such as yeast cells, cream of tartar and other proteins. More specific objectives are included in experimental section 5.4.

5.3 MEMBRANE PROCESSES AS ALTERNATIVES TO THE EXISTING CHEMICAL PROCESSES

5.3.1 PROBLEMS THAT MAY ARISE

Problems that may arise and questions that must be asked when deciding on possible suitable membrane systems are:

(i) Will fouling of membranes occur, resulting in uneconomical flux-values - especially in the case of UF membranes?

(ii) Is there the possibility of a greater positive water balance since a system by which recycling of water is possible must be used?

(iii) Are UF membranes able to withstand the abrasive nature of the wine lees effluent?

(iv) Will it be economical to make use of RO membranes to concentrate KHT solutions, especially at the high operating pressures required for RO?

(v) Will traditional RO membranes be resistant to the KHT crystals that form and how would this influence their flux?

(vi) Will it be possible to replace the existing system with a more compact and effective system?

5.3.2 MEMBRANE SYSTEM COMBINATIONS

5.3.2.1 Combined UF and RO system

Figure 5.1 shows a system comprising a UF and an RO unit.

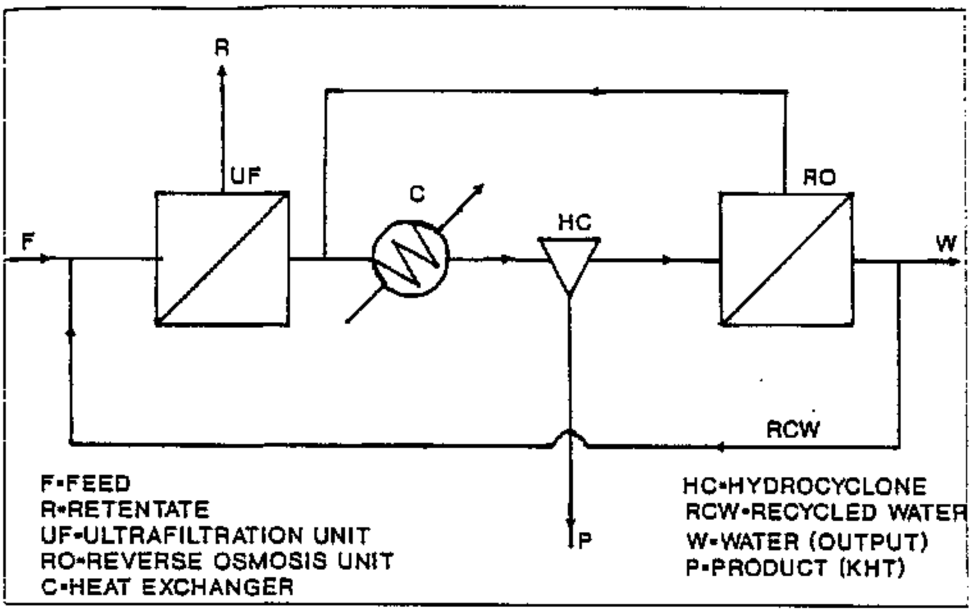


Fig. 5.1:
KHT recovery by a combined UF and RO system.

The wine-lees cake is mixed with water and concentrated by UF. The result is that a large percentage of KHT dissolves in the UF permeate and is thus isolated from the wine lees. This permeate is then concentrated by RO. As the solubility of KHT in water is very poor (see Fig. 5.2), crystals will form when the KHT reaches a concentration of 0,6% at 20 °C. A cooling system could also be installed to increase precipitation of KHT. An advantage of this system could be that clean water produced from the RO membrane unit could be used as make-up for the UF unit. However, to make the process viable it is important that the RO membranes should be efficient as far as flux and operating pressures are concerned. In this regard it is favourable that KHT has poor solubility and that the osmotic pressure of an aqueous solution thereof would be low, resulting in a low operating pressure being required.

It is also possible that a NF membrane rather than an RO membrane could be used, because KHT is a relatively large molecule with a molecular mass of 188,8. Operating pressure requirements would be lower for a NF membrane compared to an RO membrane. An experimental IPS PVOH NF membrane is available and could be used.

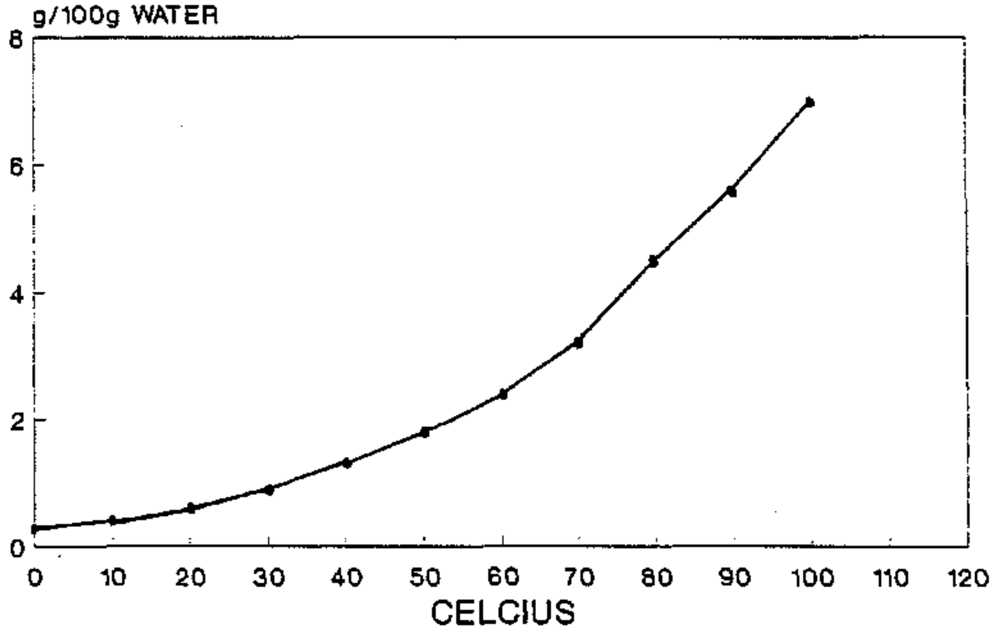


Fig. 5.2:
Solubility curve of KHT in water.

5.3.2.2 Combination of UF and chemical treatment

Another system that could be used was a combination of UF and chemical treatment (see Fig. 5.3).

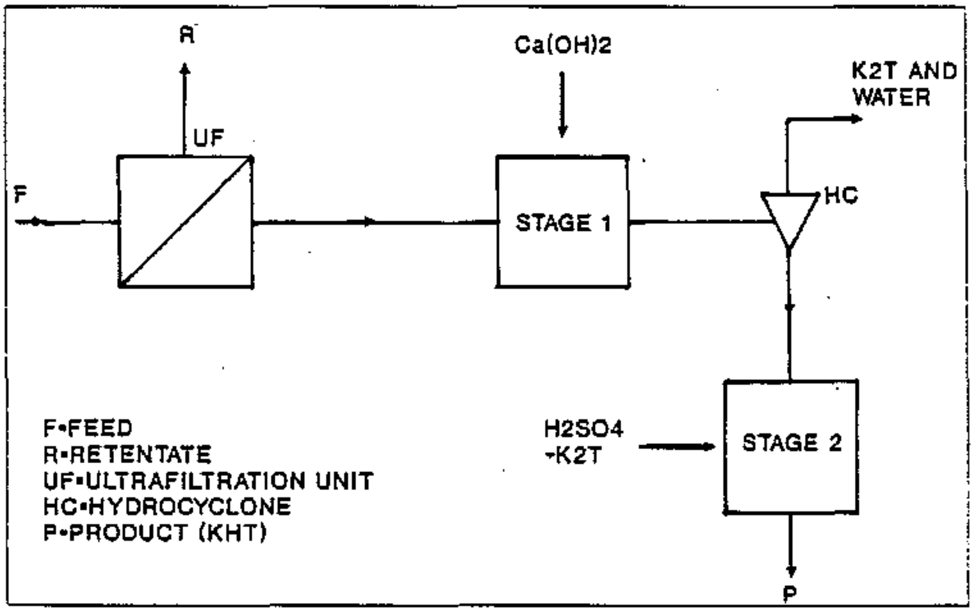


Fig. 5.3:
KHT recovery - UF and chemical process combination.

Basically, the slurry would be treated by UF to separate the yeast cells and proteins from the KHT-rich solution. The UF permeate could then be chemically treated to yield the final product.

The permeate would be treated with $Ca(OH)_2$ to form CaT and K_2T. This would again be treated with sulphuric acid to produce the product, KHT. The relevant chemical reactions are:

$$2KHT + Ca(OH)_2 \longrightarrow CaT\downarrow + K_2T + 2H_2O \qquad \text{(Eq. 5.1)}$$

$$CaT + H_2SO_4 \longrightarrow CaSO_4 + H_2T \qquad \text{(Eq. 5.2)}$$

$$K_2T + H_2T \longrightarrow 2KHT \qquad \text{(Eq. 5.3)}$$

As CaT is very insoluble in water, it would precipitate and could be collected by means of a hydrocyclone, before final addition of H_2SO_4 to form the product.

5.3.2.3 Other combinations

Combinations of the two abovementioned systems can be used in conjunction with the existing chemical process. Use of a membrane separating system, as indicated in the above two methods, could improve efficiency.

5.4 EXPERIMENTAL

5.4.1 SPECIFIC OBJECTIVES

The specific objectives of the experimental investigation were to:

(i) determine the number of cycles required to wash the slurry with water in order to extract most of the KHT present;

(ii) determine the optimum operational conditions, for example, temperature, pressure, linear velocity, etc.;

(iii) determine the maximum solids concentration of the wine-lees slurry on which the membrane would still operate successfully;

(iv) test different UF and RO membranes in order to find that one with the best combination of flux and retention properties;

(v) find the most effective membrane-cleaning procedure for this application; and

(vi) determine the effect of concentration polarization, gel-layer formation and fouling on the membrane surface.

5.4.2 PLANNING OF EXPERIMENTS

5.4.2.1 UF membrane testing

A range of PS UF membranes was tested on single-cell test-rigs. Wine lees of various solids concentrations were made up for testing. Prior to the testing, the lees were first mixed at high shear rates, thus reducing the lees to a fine suspension.

In order to accurately calculate the concentrations of solids, the water content of the wine lees cakes, as received from the factory, was determined. This was done by weighing samples before and after drying them in a vacuum oven.

The UF membranes were tested in diafiltration mode in a six-cell test-rig at 500 kPa and at a linear velocity of 2 m/s. At first the temperature was kept constant at 30 °C, but this was later increased to 35 °C to obtain higher fluxes and to allow more of the KHT to dissolve.

5.4.2.2 RO membrane testing

Permeate collected from UF membranes was used to test RO and NF membranes. The KHT solution was concentrated to a point at which precipitation would readily take place. It was important to determine the optimum operating temperature of the system. A lower operating temperature would result in more rapid precipitation of KHT crystals, but at the same time higher operating temperatures would result in higher permeate fluxes which in turn would result in lower operating costs.

RO membranes (CA) and NF membranes (PVOH and CA) were tested on the KHT solution.

5.4.3 KHT CONCENTRATION DETERMINATION

KHT concentration was determined by NaOH titration.

5.5 RESULTS

5.5.1 UF MEMBRANE TEST RESULTS

The purpose of separation by the UF membranes was to retain suspended solids, yeast cells and proteins, to allow easy precipitation of KHT during the concentration phase that followed. UF membranes with different MMCO's (including the commercial 719 membrane) were tested on wine lees containing various solids concentrations, namely 1,7%, 2,6%, 5% and 10% and results are shown in Figures 5.4 to 5.7.

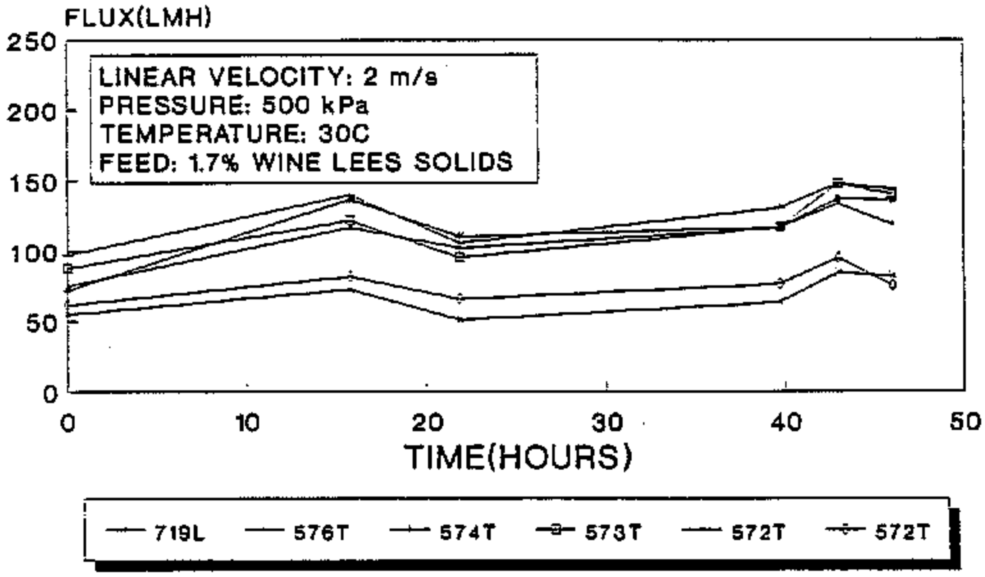


Fig. 5.4:
Flux performance of different UF membranes operated on a 1,7% wine lees solids slurry.

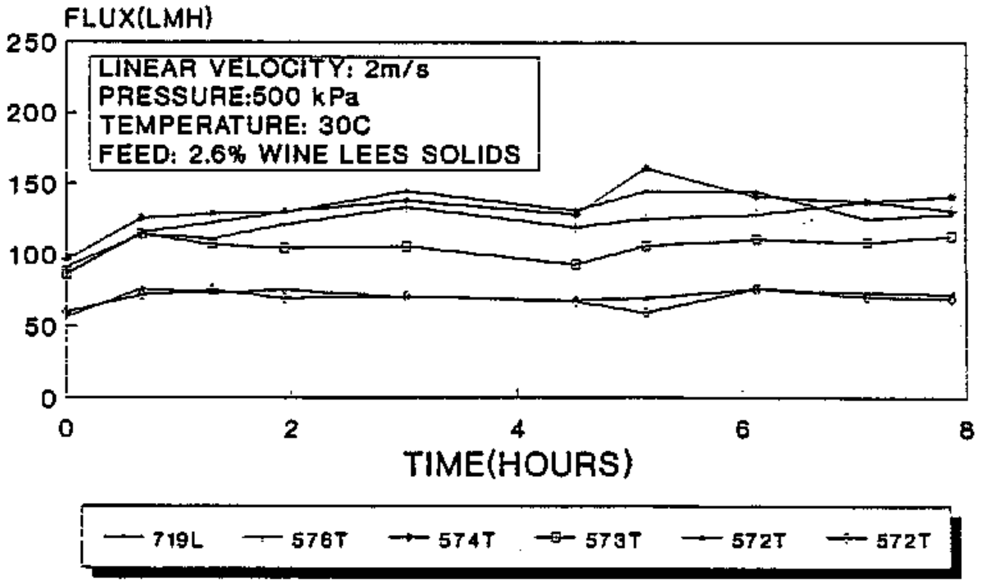


Fig. 5.5:
Flux performance of different UF membranes operated on a 2,6% wine lees solids slurry.

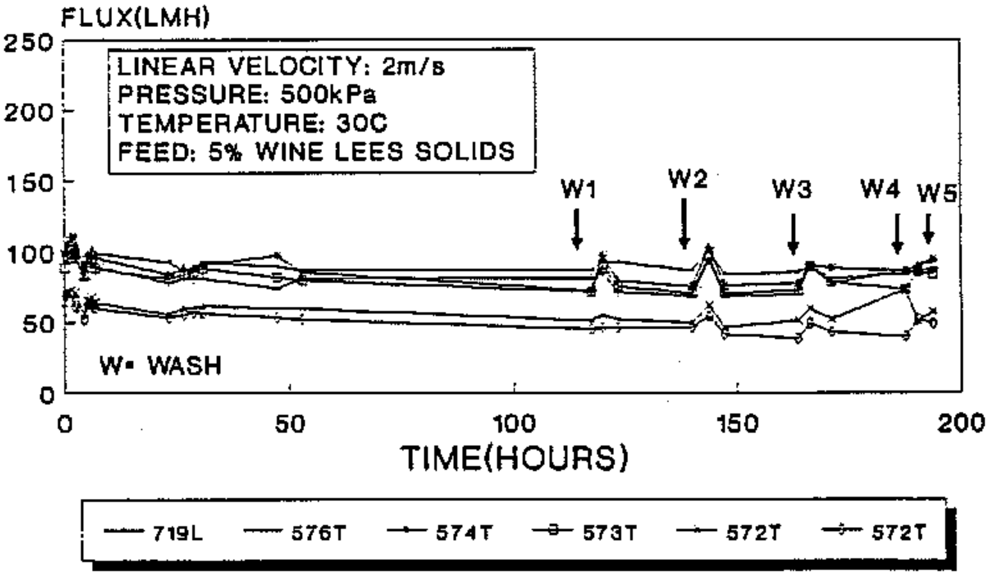


Fig. 5.6:
Flux performance of different UF membranes operated on a 5% wine lees solids slurry.

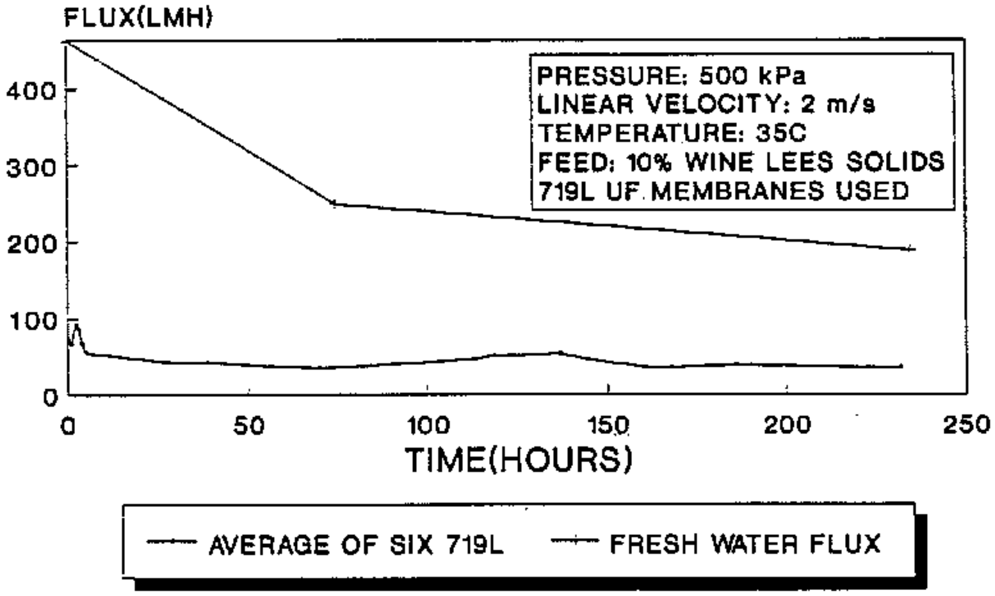


Fig. 5.7:
Flux performance of UF membranes operated on a 10% wine lees solids slurry.

The MMCOs of the PS UF membranes tested on PEG were:

719	60 000 dalton
572T	6 000 dalton
573T	35 000 dalton
574T and 576T	40 000 dalton

Although difficulties were encountered with equipment during testing on high solids concentrations, no visible damage was done to the membrane surface. Permeate fluxes stabilized within the first 50 h of operation, and no permanent fouling occurred during the process. Only fresh-water washes were done during the experiments.

Although there was a difference in quality of the permeate produced by the different membranes, the fluxes tended to stabilize at approximately the same value of 50 lmh. Hardly any difference in stabilized flux of the 5% solids and 10% solids was evident.

Diafiltration was applied when the wine lees slurry was alternately concentrated and diluted with clean water, and the permeate was collected and introduced to the RO system. This was done five times with the 5% solids slurry to ensure that all KHT present could be collected in the permeate. The feed and permeate were analyzed after each "wash" ("wash" meaning alternate concentration to collect permeate and dilution with clean water) to determine the KHT content (see Fig. 5.8). From the data it was clear that a certain percentage of the KHT was retained. This was either caused by gel-layer formation on the membrane surface or by the affinity between KHT and the yeast cells. Figure 5.8 also shows an exponential increase in retention of KHT, when the percentage of KHT in the feed decreased. (This was important when deciding at which point washing of the slurry had to be terminated in order to achieve maximum efficiency.)

Similar results were obtained when a 10% solids slurry was used as feed (see Figs. 5.7 and 5.9). The main purpose of the 10% solids tests was to determine whether the membrane could physically withstand the slurry, and to determine whether there would be a substantial reduction in permeate flux. Permeate from this experiment was collected for further trial tests on NF and RO membranes. Only 719 membranes were used in this test, and three slurry "washes" were done in order to collect permeate for the RO operation.

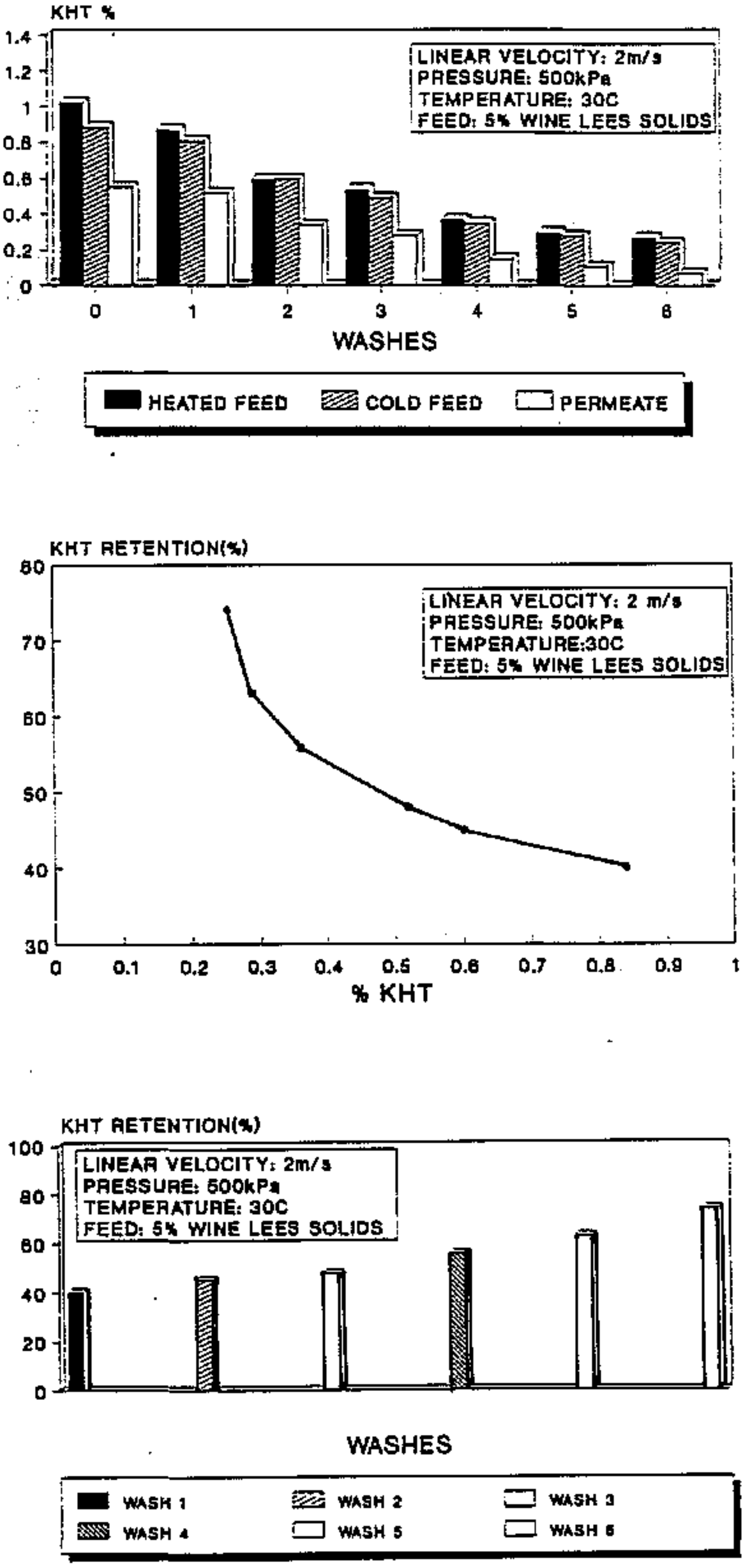


Fig. 5.8:
Performance of different UF membranes operated on a 5% wine lees solids slurry.

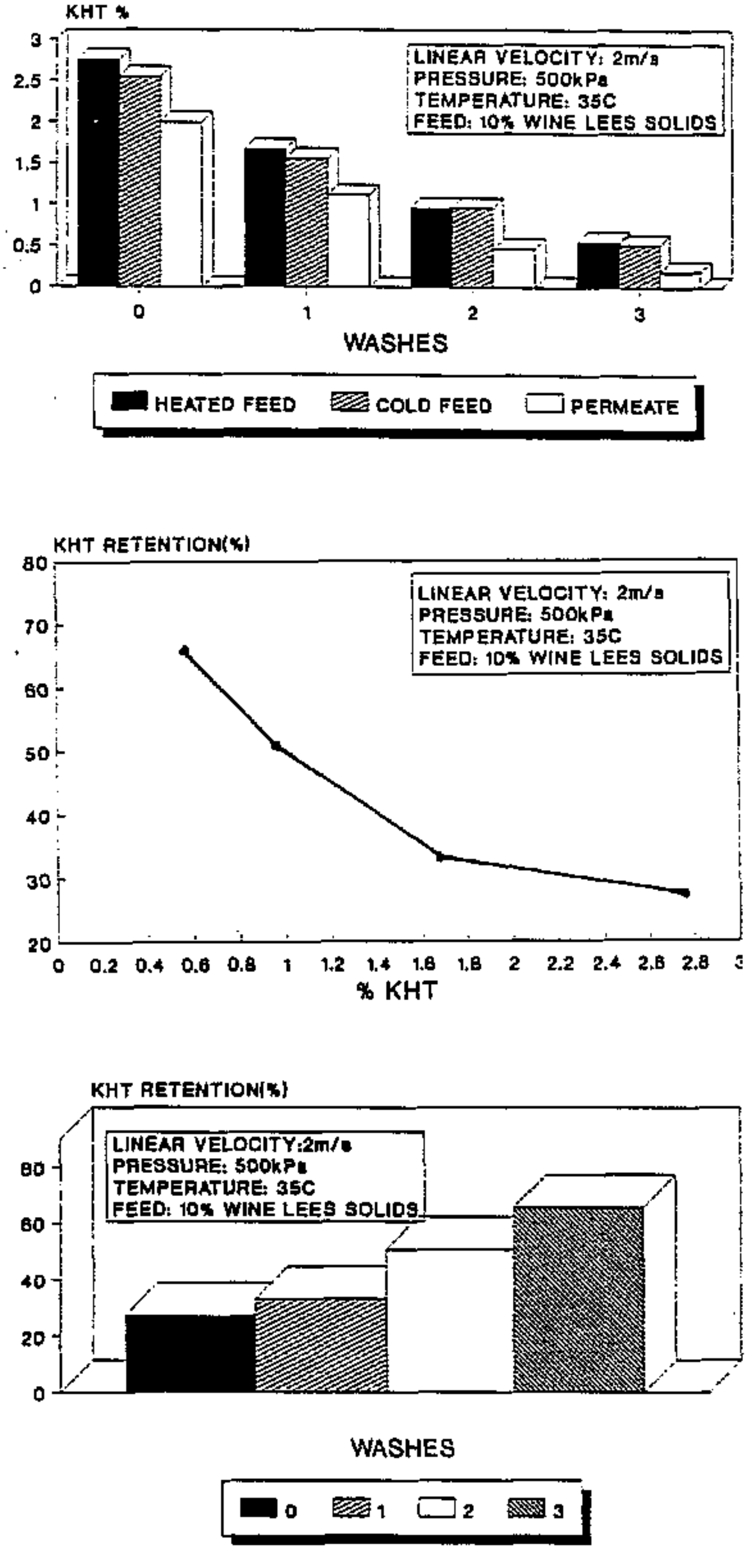


Fig. 5.9:
Performance of UF membranes operated on a 10% wine lees solids slurry.

5.5.2 RO MEMBRANE TEST RESULTS

Permeate collected from the 10% wine lees solids was used as feed to test different RO and NF membranes. Results are given in Figures 5.10 and 5.11. When the UF permeate was concentrated to 85%, precipitation of KHT crystals was rapid.

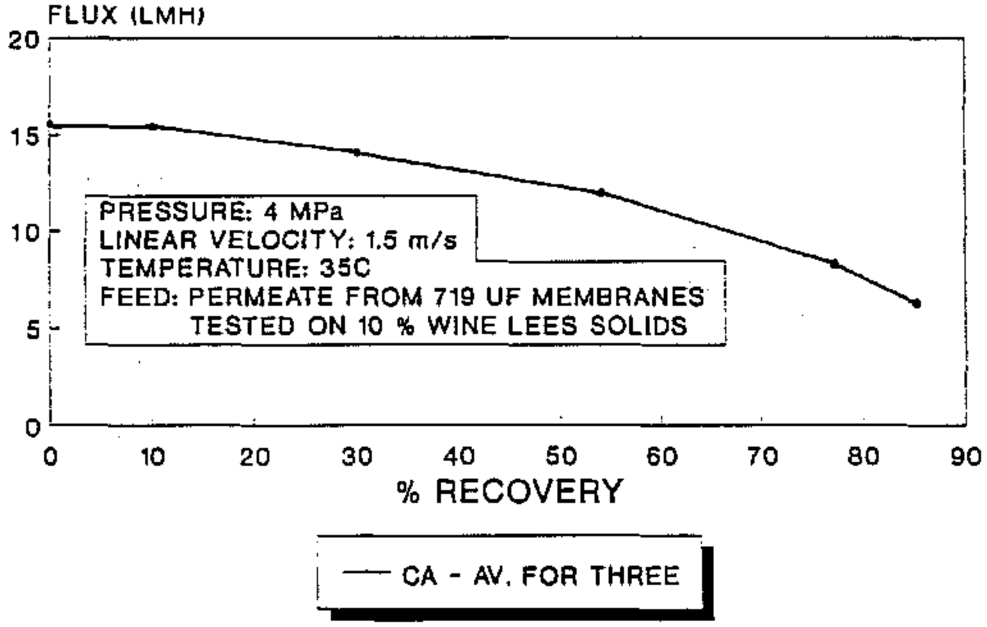


Fig. 5.10:
Performance of reverse osmosis membranes (CA) operated on permeate collected from UF.

Figure 5.10 shows a decline in flux with increasing recovery when CA RO membranes were tested on the UF permeate. This was unexpected because KHT precipitation should have maintained the real concentration at a constant level. However, the UF membranes still allowed smaller proteins to pass through and, because of this, concentration of these proteins occurred when RO or NF was applied and a reduction in permeate flux resulted. Optimization of operating costs will have to be done to determine at what concentration the operation will be viable. Another option would be to make use of a lower MMCO UF membrane and subsequently reduce the amount of smaller proteins in the permeate, or even eliminate them, although decreasing the MMCO of the UF membrane could result in an increase in KHT retention.

The PVOH NF membrane had a pure-water flux-value more than double that of a standard CA RO membrane, and therefore higher fluxes were expected from the NF membrane during operations on the KHT solution. After the operation was started, however, the flux immediately decreased to unacceptable levels and the membranes were therefore removed. An experimental NF CA membrane (code: 6BC84) was tested towards the end of the experiment and although conductivity retention was lower than that for the CA membrane, KHT tests conducted on the permeate showed that only small traces of KHT were present. The flux through this membrane was, however, relatively high and further tests are being conducted to determine the value of the stabilized flux.

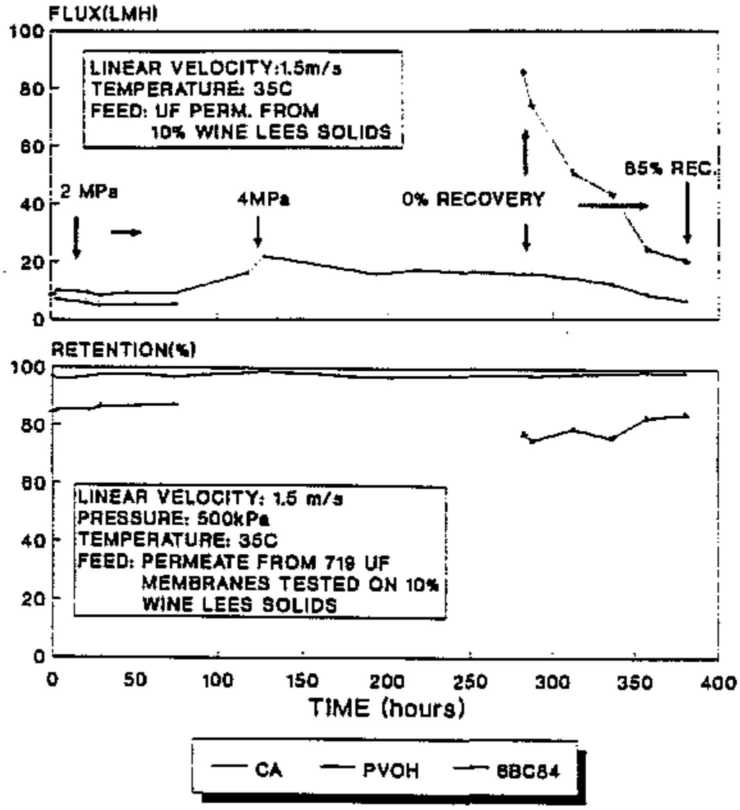


Fig. 5.11:
Flux and retention performances of RO and NF membranes operated on permeate collected from UF.

Figure 5.11 shows a dramatic reduction in flux of the experimental CA NF membrane. The reason for this was, first, the increase in feed concentration, and, second, that the NF membrane was tested together with a RO membrane, and subsequently tested at an operational pressure of 4 MPa. The normal operating pressure of a NF membrane was much lower (approximately 2 MPa) and compaction of the membrane occurred at the elevated pressure.

300 g KHT were collected in the above experiment after the concentrated KHT solution had been cooled to 4 °C. Originally 5 kg wet lees were used to make up the 10% solids slurry. The wet wine lees (in cake form containing 50% water) contained 15% KHT and calculation showed that approximately 40% of the KHT originally present, was recovered from the lees. This amount could be increased if more washes were given in the UF stage.

5.6 DISCUSSION

UF membranes were tested on wine lees containing various solids concentrations, namely 1,7%, 2,6%, 5% and 10%. The purpose of using the UF membranes was to retain suspended solids, yeast cells and proteins, and to allow easy precipitation of KHT from the UF permeate during the concentration phase (with RO or NF) that followed.

Permeate fluxes stabilized within 50 h at 50 lmh and the following were found: (i) the high solids concentrations in the feed caused no visible damage to the membrane surface; (ii) no permanent fouling occurred during the process (the membrane surface appeared clean and shiny with no organic material deposited on it); and (iii) only fresh-water washes were required.

Diafiltration was applied, meaning that the wine lees slurry was alternately concentrated and diluted with clean water, and the permeate was collected for introduction into the RO system. From analyses of the feedwater and the UF permeate it became clear that a certain percentage of the KHT was retained by the UF membranes. Tests showed an increase in retention of KHT, when the percentage KHT in the feed decreased. This could be either the cause of a dynamic gel layer being formed on the membrane interface or because of the affinity of KHT for the yeast cells and proteins being circulated.

Permeate collected from the 10% wine lees solids UF feed was used to test different RO and NF membranes. When the UF permeate was concentrated to 85% using RO, precipitation of KHT crystals took place rapidly. It was found that a decline in flux occurred with increasing water recovery. This phenomenon was unexpected because the KHT precipitation should have maintained the real concentration at a constant level. However, the UF membranes still allowed smaller protein molecules to pass through and, because of this, concentration of these proteins occurred when RO or NF were applied, resulting in a reduction in flux. Optimization of operating costs will have to be done to determine at what concentration the operation would still be viable. Another problem caused by proteins in the UF permeate was the inhibition of crystal growth when the concentration process started.

After testing various RO (CA) and NF (PVOH and CA) membranes on the UF permeate, it was found that the experimental NF CA membrane (code: 6BC84) gave the best results with fluxes more than double that of the RO membranes.

The test results indicated the possibility of eventually using a UF/NF system. The proposed system would consist of a mixing unit, an UF unit and a NF unit. The wine lees solids would enter the mixing unit, where water would be added and a high shear rate blender would homogenize the slurry. After filtering out sand in the slurry, an UF unit would separate the wine lees solids and most of the proteins from the KHT in solution. The UF permeate would then enter into a NF unit where concentration and subsequent precipitation of KHT would occur. It must be borne in mind that the KHT solution entering into the NF system contains other contaminating salts, ions and smaller proteins. It would therefore not be wise to keep on concentrating without bleeding, in order to partially discard the saline solution while a fresh batch enters into the system. For this reason the best way to operate the NF unit would be on a batch basis. The question of operating temperature in the NF system is an important one. A high operating temperature would result in a greater membrane flux. The KHT would, however, be more soluble and precipitation would not be as effective as in the case of lower operating temperatures.

It was decided that UF and NF membranes should be installed on a pilot plant scale at the factory, to determine the viability of a full-scale operation. A NF membrane test unit was therefore designed and constructed for installation at the factory at Brennochem. See Figure 5.12.

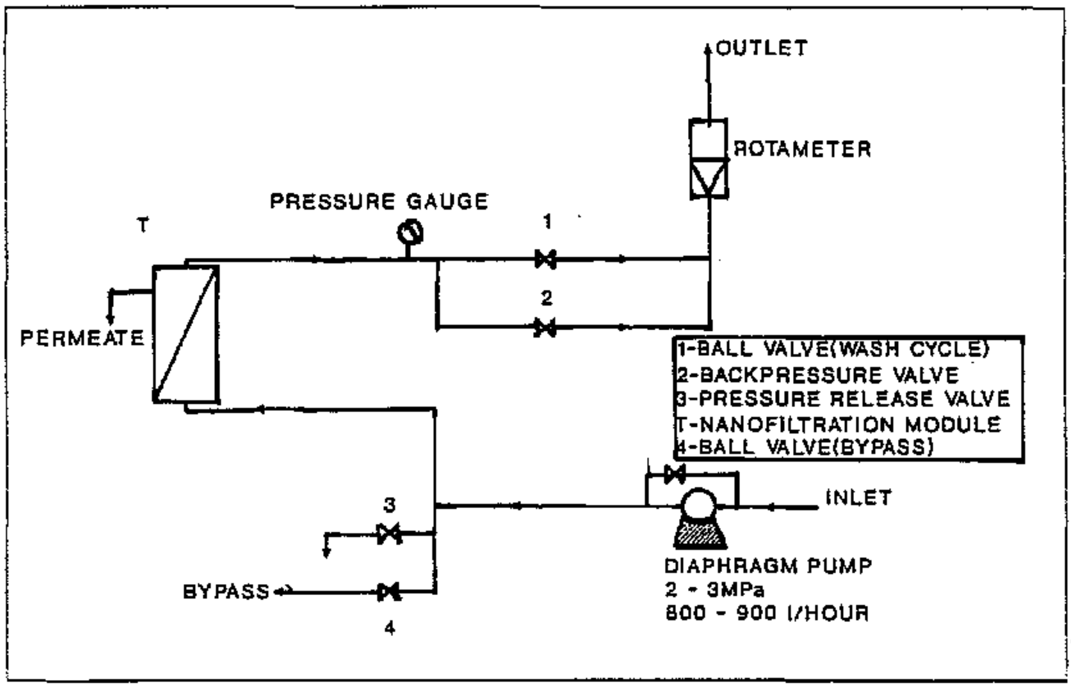


Fig. 5.12:
NF membrane test-rig design.

Experimental NF membranes were assembled in a 1 m module and installed at the factory. The membranes were to be tested on "crystal water" which is an existing KHT-rich stream at the factory and which compares well with the permeate from UF membranes that have been operated on a wine lees slurry in the laboratory. Various tests still need to be conducted in the NF field to find the most suitable membrane for this application. Modules containing different NF membranes are yet to be installed in the test unit.

An UF test unit should also be installed at the factory, and at a later stage be operated in conjunction with the existing NF unit. It should be stressed that the wine lees slurry entering into the UF membrane system should be free of sand and lumps of wine rests. Sand could be detrimental to the membranes as well as to the pumping systems, while lumps of yeast could cause blockage of the tubular membranes. For this reason it would be advantageous to make use of a homogenizer (i.e. a blender) and a hydrocyclone or centrifuge for pretreatment to eliminate the problem of lumps and sand particles.

The entire operation will first have to be done on a pilot-plant scale in order to eliminate possible problems.

5.7 CONCLUSIONS

The objective of this study was to determine whether membrane processes could be applied in the fractionation of wine lees to produce usable by-products such as yeast cells and cream of tartar (potassium bitartrate).

UF membranes were operated in diafiltration mode in order to "wash" the wine lees slurry at different solids concentrations. The KHT-rich permeate collected from UF was then concentrated using RO or NF to enable precipitation of the product (KHT).

Tests were conducted with experimental and commercial UF membranes at different solids concentrations. The wine lees slurry was alternately concentrated and then diluted with clean water until most of the KHT present in the feed was removed. UF membrane test results showed that while fluxes stabilized at a relatively high level of 50 lmh, no permanent fouling occurred during the tests. The permeate was collected for testing on RO and NF membranes.

Tests were conducted on the UF permeate using a commercial RO membrane and two different types of NF membranes. An experimental NF membrane gave good fluxes with KHT retentions of above 80%.

A NF membrane test unit was designed for installation at the factory at Brennochem. Experimental NF membranes were cast into a 1m module and installed at the factory. Various tests still need to be conducted in the NF field to find the most suitable membrane for this application.

CHAPTER 6

RESTORATION OF MEMBRANE PERFORMANCE

6.1 BACKGROUND

The economic viability of a membrane operation is totally dependant on membrane performance and high permeate flux rates at acceptable retention values is the goal of any plant operator or designer. However, too often this ideal is removed from the realities of plant operation. Regular cleaning of membranes is the recommended procedure to maintain the performance of membranes not only of those that operate on relatively clean water (e.g. borehole water or well pretreated streams) but also those that operate on contaminated water (e.g. industrial effluent or untreated sea water). It is for this reason that the development of suitable cleaning regimes to ensure steady product volume rates should be very much a part of any pilot plant or bench study on the application of membranes. Besides maintaining membrane performance by adopting a regular and effective cleaning protocol, there is another approach by which membranes performance may be restored once it has deteriorated. This approach may be described as the restoration of membranes performance by means of a supplemental polymer coating.

In addition to studies on the applications of membranes, the problem of membrane performance restoration was to received attention, both through the development of suitable cleaning regimes and the application of polymer coatings. These studies were initiated from outside the programme, owing to the following:

(i) problems were experienced with permanent flux decline of membranes operating on an abattoir effluent stream and alternative cleaning regimes had to be sought;

(ii) cleaning strategies were being investigated on capillary membranes used in the pretreatment of sea water for RO desalination, and the question was raised as to whether enzymes could be used effectively to restore permeate flux; and

(iii) the question was raised as to whether techniques could be devised to restore the performance of spiral wrap elements which had deteriorated to levels at which they were unfit for use.

Aspects of physical and chemical restoration of membrane performance were to be investigated. Two distinctly separate methods of membrane performance restoration were to be investigated:

(i) cleaning regimes; and

(ii) supplemental polymer coatings.

6.2 CLEANING OF PES TUBULAR UF MEMBRANES: AN ABATTOIR CASE STUDY

6.2.1 INTRODUCTION

This study was undertaken at the request of the Steering Committee of a WRC Research and Development programme entitled:

Transfer of waste water treatment management technology to the meat processing industry (Project no 239, 1991).

The waste stream generated by a red-meat abattoir represents, on the one hand, a serious potential pollutant with chemical oxygen demand (COD) levels as high as 12 000 mg/l and with soluble phosphate levels as high as 80 mg/l. On the other hand, however, the stream also contains a potentially valuable source of bio-material. Conventional biological treatment with anaerobic and aerobic digestion is used very successfully to produce an effluent stream of suitable quality for discharge into the environment [Ref. 6.1]. Such a process has, however, the disadvantage that it requires a relatively high degree of skilled management to achieve stable operation in the face of the highly variable nature of the effluent stream. Furthermore, its purpose is to degrade biological material, so that it offers no prospects for recovering such materials as a by-product.

Membrane filtration offers a potential solution for the treatment of abattoir process and rinse water effluent. The permeate from a membrane plant would be suitable for re-use in various non-critical areas of the abattoir, or for direct discharge or for discharge to municipal sewers. The increased concentrations in the retentate stream, compared with the raw effluent, improve the economic prospects of bio-material recovery processes, such as composting or rendering. The South African Abattoir Corporation (ABAKOR) together with the South African Water Research Commission (WRC) have been investigating the use of ultrafiltration (UF) and reverse osmosis (RO) as an alternative to conventional biological treatment. In a two-stage pilot plat supplied by Membratek, medium molecular mass cut-off tubular UF membranes were used to treat screened process wastewater before further treatment with tubular CA RO membranes.

6.2.2 OBJECTIVES

The main objective of the study on the cleaning of membranes operated on abattoir effluent was to determine to what extent chemicals, known to the abattoir industry, and used by them for sanitizing purposes, would be effective in restoring membrane productivity. It was also important to determine to what extent these chemicals might be harmful to the membranes themselves.

For the purpose of this study, a set of 2,4 m-long 13 mm tubular 719-series poly(ether sulphone) membranes, that had been operated on effluent at the abattoir at Cato Ridge, were obtained from Membratek.

6.2.3 EXPERIMENTAL

The membranes received were severely fouled. The surfaces of these membranes were coated with a yellow/brown layer of deposit, so thick in some areas, that it looked like apple-peel. The heavy deposit was not evenly distributed over the membranes; the fouling was noticeably more severe in certain areas than in others. Furthermore, in some locations the deposit had formed along a half-section of the tube. (This indicates that the operation of the membrane plant had been interrupted without the process fluid having first been rinsed from the system. If enough time was allowed before restart, proteinaceous material would coagulate and settle inside the membrane, with an obvious deleterious effect on permeate flux).

The outside of all the membranes (i.e., the polyester substrate material), was tinted a light yellow. There was, however, no indication of dark-staining of the support fabric, which was good reason for the belief that the membranes were still performing well.

EDAX analysis and melt-point determination were used to analyze the fouling layer. No biotopsy was attempted.

6.2.3.1 EDAX analysis

An EDAX analysis of scrapings taken from the membrane surface pointed at the presence of sodium, silicon, phosphate, sulphur, potassium, aluminium, calcium, iron, copper and zinc.

These salts may be bound into the deposits on the membrane surface by hydrogen-bond formation and/or complexation with proteinaceous material. Use of a cleaning agent should therefore show some effect in flux restoration if it is capable of interfering with the mechanism by which proteins are insolubilized. This may explain why alkaline EDTA, with its strong sequestering properties, is effective in restoring product flux to some degree [Ref. 6.2].

6.2.3.2 Melt-point determination

Animal fat is one other constituent of an abattoir effluent which can cause severe fouling of a hydrophobic membrane. Lipids give rise to particular problems because of their low solubility and hydrophobicity (membrane adsorption potential).

A thermal analysis was performed by DSC (differential scanning calorimetry) to see whether there was any substance on the membrane which could give a thermal event (such as melting point/range, low-energy mechanical transitions, etc.) and thus give an indication of its make-up/character.

The DSC Thermograph showed a broad melting peak at temperatures between 25 and 70°C with a peak melting point of 50°C. This type of peak is characteristic of low molecular mass substances such as waxes and fats. This does suggest that some of the fouling material adhering to the membrane contains some form of animal fat.

6.2.3.3 Determinations of effectiveness of cleaning agents

The experiments that were conducted to determine the effectiveness of cleaning materials, concentrated on the use of two commercially available cleaning agents. The one was a proteolytic enzyme-based formulation (used in conjunction with sequestering, wetting and emulsifying agents, all specially formulated for use in the abattoir industry), and the other was a chloralkali sanitizer..

Table 6.1 gives information on the cleaning agents that were used and their recommended concentration levels.

Table 6.1: Cleaning agents for soiled abattoir-operated UF membranes

Product name[a]	Comments	Concentration	Constituents
Zymex	Enzyme-based detergent used in 1:1 ratio with Alkazyme	1 to 3%	detergents stabilized enzymes non-anionic wetting agents emulsifiers
Alkazyme	Synergizer, used in 1:1 ratio with Zymex	1 to 3%	mild alkalis sequesterants water softeners
Sanoklor	Sterilizer (peptiser)	1 g/l	mild alkali chlorine
Biosolve	Cleaner	5 to 20 ml/l	mild alkalis penetrants emulsifiers grease cutting agents

a. Technical Brochure : Syndachem Sales (Pty) Ltd.

Pure-water flux (PWF) rates were used to determine the effect of a cleaning operation in restoring the performance of the membranes. In this test, the membranes were loaded into tubular test cells, and operated on RO tap water feed at three different pressures. The linear-flow velocity was kept at 0,5 m/s to maintain low pressure drops across the test-loop. The temperature was controlled at 20°C unless otherwise stated.

Figure 6.1 shows a plot of some results to give an indication of the extent to which the PWF's of the membranes were affected by the presence of fouling layers.

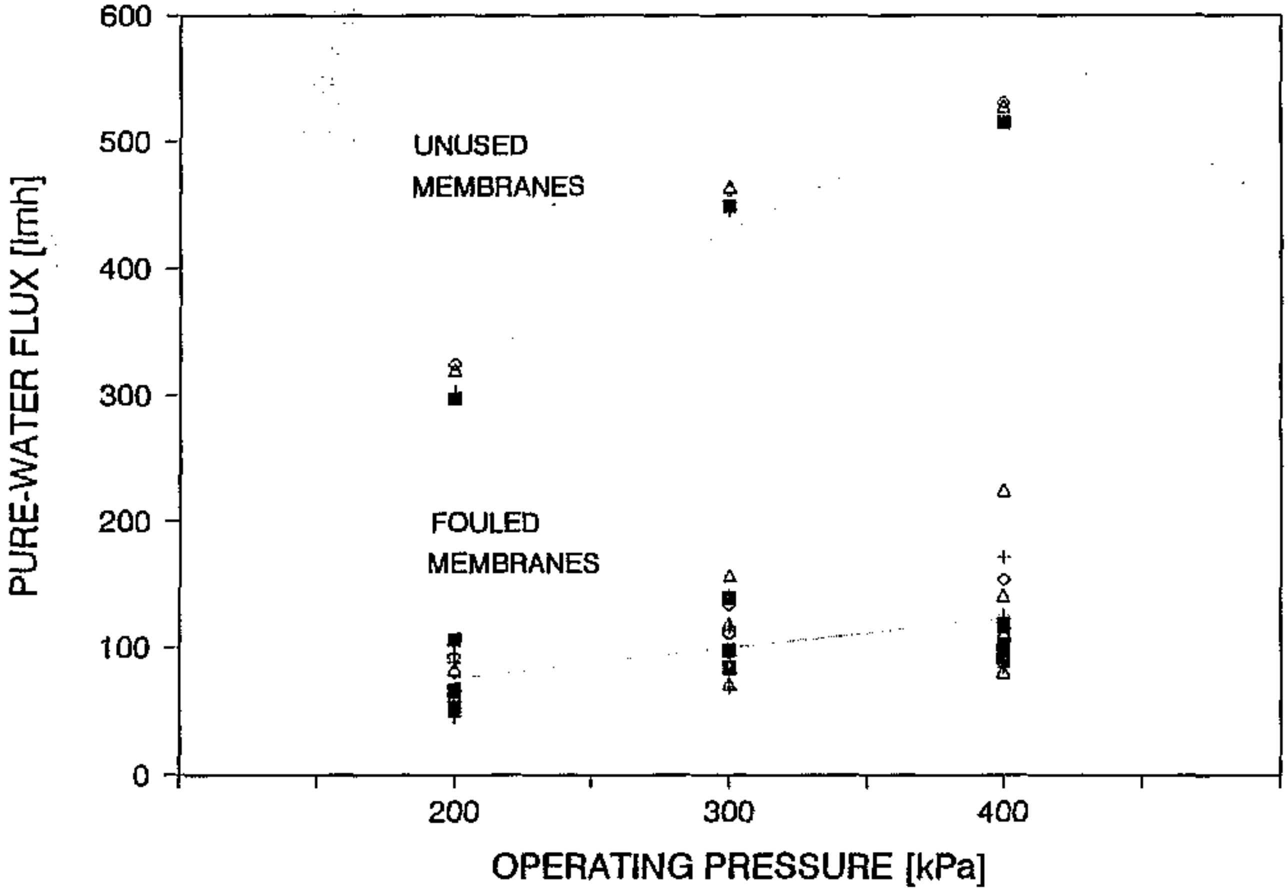


Fig. 6.1:
Pure-water flux base-line comparisons of PES membranes.

6.2.3.4 Cleaning sequences

Two methods were used to determine the effectiveness of the cleaning agents, the one is referred to as the **static** rinse, and the other as the **dynamic** rinse.

A. Static rinse

Static rinses were performed by cutting fouled membranes into short lengths (100 mm) and allowing these to soak in the cleaning agents in a glass beaker while stirring for extended periods. The cleaning agents were replaced regularly with freshly made-up solutions.

Static rinses were also performed on longer membrane sections (500 mm), by loading the membrane into a test cell, and half-filling the cell with a particular cleaning agent. The test cell was shaken for 10 min, after which the membrane was rinsed and retested for its pure-water flux performance.

B. Dynamic rinse

In the dynamic test the membranes were loaded into the test rack (four 500 mm-long membranes in series), where all the rinses and evaluations were performed without disturbing the membranes.

A 5 l vessel was used as a feed tank for the cleaning solutions which were circulated through the cells by means of a centrifugal pump at a linear velocity of 2,5 m/s and inlet pressure of 100 kPa for either 30 min (for enzymatic agents) or 10 min (for chloralkali). The 5 l tank was not equipped with a cooling coil, and the temperatures increased steadily during the period. The temperature of the circulated solution increased from about 20°C to 55°C over a 30 min circulation period.

The pure-water flux of as-received membranes (i.e., fouled membranes) showed a large deviation from the mean. For this reason the membranes were compared on the basis of their normalized fluxes (i.e., the PWF of each as-received membrane was taken as unity).

C. Sponge ball rinse

After each cleaning cycle, four sponge balls were released into the test line. Air was introduced into the test loop after the sponge balls had been inserted; this resulted in a very effective sponge-ball/air combination wash.

6.2.4 RESULTS AND DISCUSSION

In the first experiments, in which the membranes were soaked and gently stirred in a 3% solution of the proteolytic enzyme and synergizer, it was noticeable how the foulant layers swelled and become dislodged from the membranes under the gentle stirring action. The highly swollen deposited layer could easily be scraped from the surface; this was, however, not possible once the membranes were allowed to dry out. Although the surfaces of the membranes were never touched, the photograph in Figure 6.2 shows clearly that enzymes are capable of cleaning the membranes (see lower half of Table 6.2 for a key to Fig. 6.2).

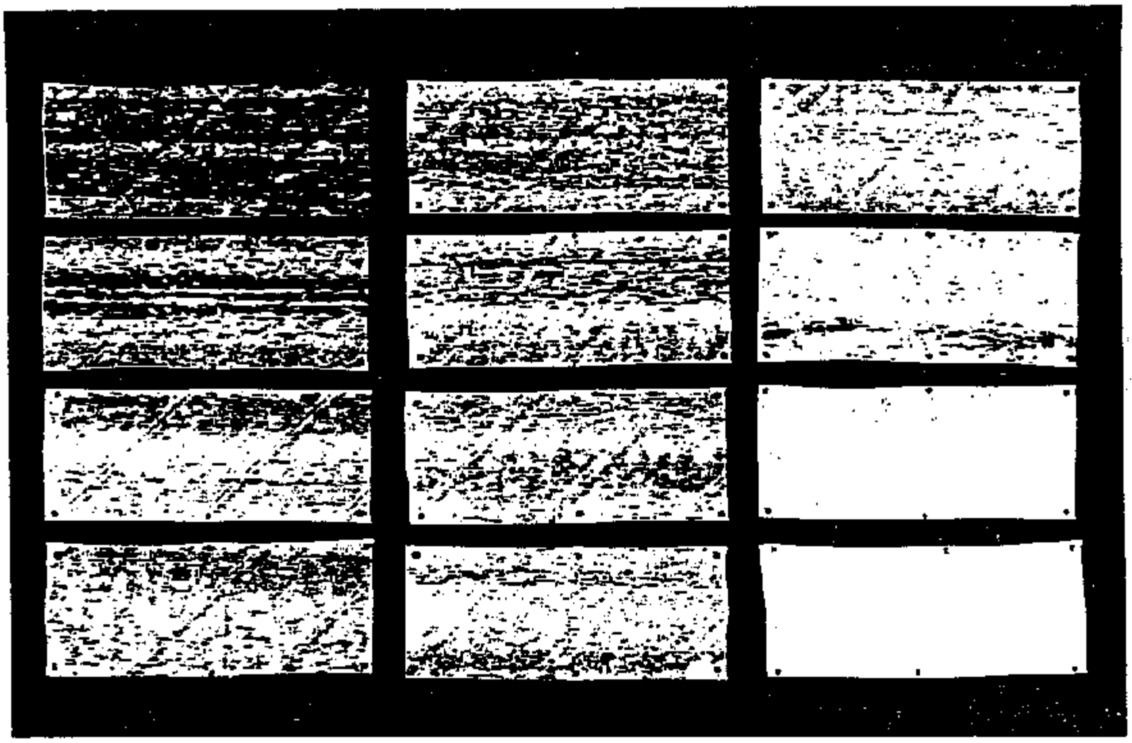


Fig. 6.2:
Photograph of membranes subjected to a proteolytic enzyme/synergizer cleaning solution.
(See Table 6.2 for a legend to the figure.)

In Table 6.2 a record is given of the conditions of this experiment, and of the total duration (hours) of the experiment. The experiment was conducted to determine whether the enzymatic cleaning agents would have any short-term detrimental effect on the mechanical performance of the membranes. The tensile tests that were performed on an Instron machine on samples of the membranes gave no indication that the membranes suffered any mechanical damage due to possible hydrolysis of the substrate membrane weld-seam. This supports the conclusions of another study, where similar membranes were subjected to pH 10 solutions for periods up to 1 000 h, with no noticeable effect on membrane performance [Ref. 6.3].

Table 6.2: Membrane exposure to a 3% enzyme/synergizer solution

Sample no	Fresh solution contact time (h)	Total accumulated contact time (h)	Solution pH	Temp. (°C)
1	17,0	0	9,9	25
2	6,5	23,5	10,3	23
3	17,0	40,5	10,4	24
4	6,5	47,0	10,5	24
5	65,0	112,0	9,2	23
6	6,5	118,5	10,1	22
7	16,5	135,0	10,2	22
8	24,0	159,0	10,2	22
9	7,5	166,5	10,2	23
10	16,5	183,0	10,2	22

Fouled membrane
sample no 1
sample no 2
sample no 3
sample no 4
sample no 5
sample no 6
sample no 7
sample no 8
sample no 9
sample no 10
Unused membrane

In Figure 6.3 the pure-water flux performances of membranes which underwent a 10 min static rinse are compared with those treated with a batch of mixed detergents. The 3% solution used was made up from an aqueous mixture of 1% each of the triethynolamine salt of dodecyl benzene sulphonate, sodium laurel ether sulphate, ethoxylated nonyl phenol and triethanolamine (pH 9,1).

Figure 6.4 shows the effect of a 10 min static rinse with a 3% enzyme/synergizer solution on the PWF performances of the fouled membranes.

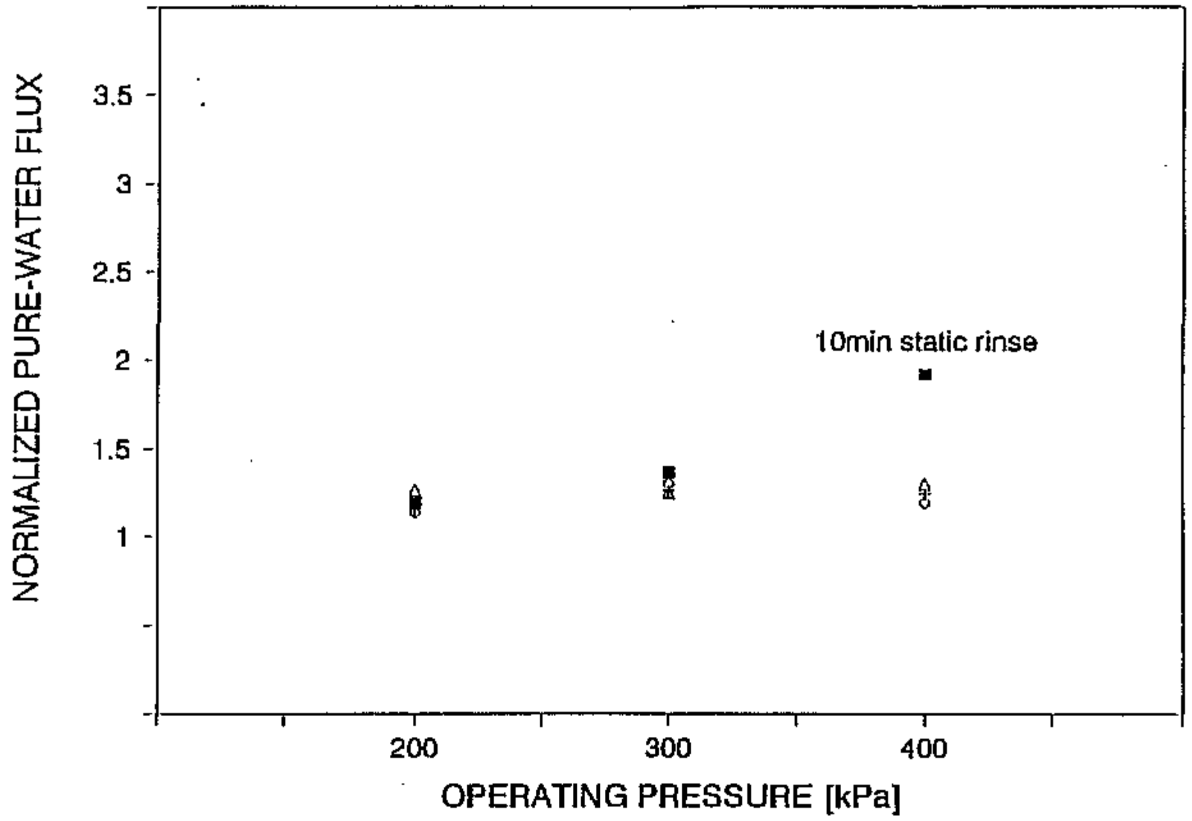


Fig. 6.3:
PWF performance of fouled membranes treated with mixed detergents.

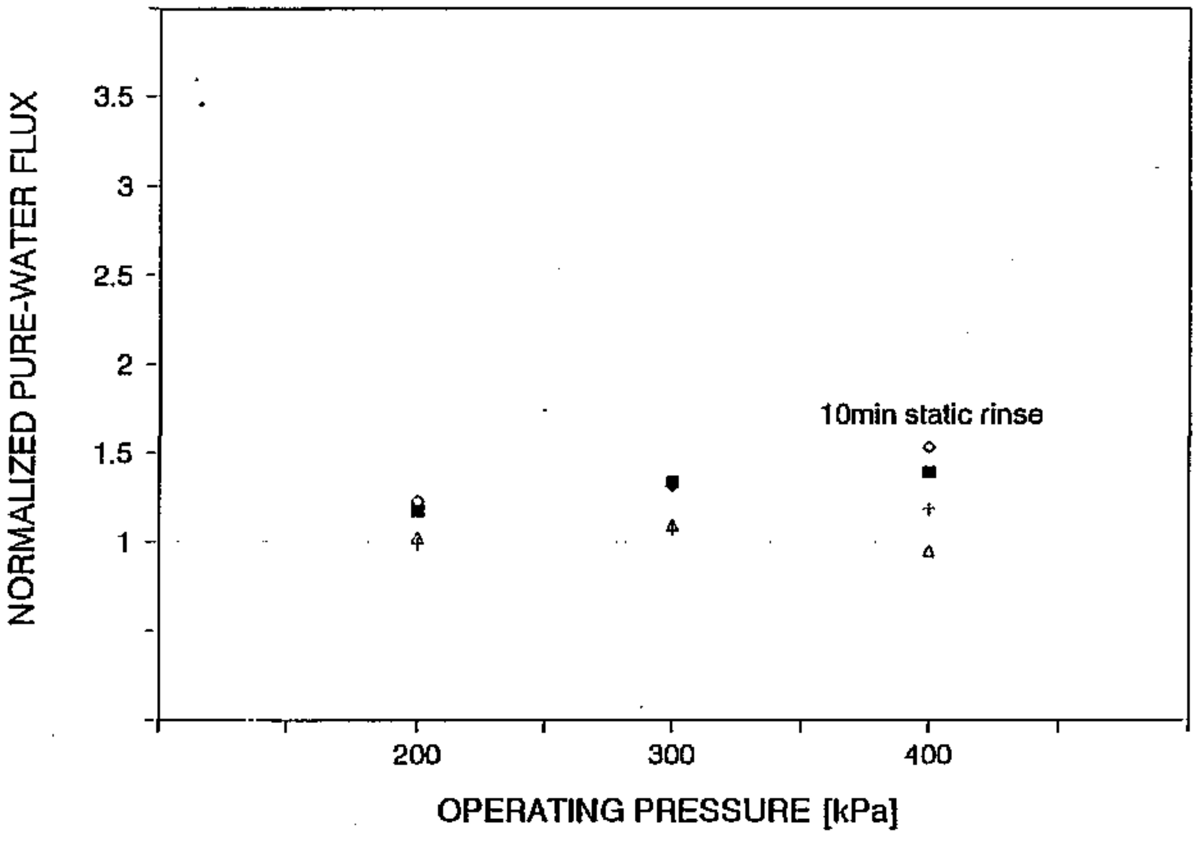


Fig. 6.4:
PWF of fouled membranes exposed to enzyme treatment.

By comparison, the cleaning operations conducted in the dynamic mode, in which the temperature was allowed to increase due to circulation, had a more pronounced effect on improving the PWF performance of the membranes than the static rinse did. Figure 6.5 shows the two-fold increase in PWF obtained with a 30 min enzyme/synergizer treatment at temperatures higher than 20°C. The role which the sponge balls played in entraining the deposits should not be overlooked.

A similar improvement resulted when membranes were treated with a chloralkali peptizing solution. (At the concentrations used, the solution contained 150 mg/l free chlorine.) Figure 6.6 shows the results of a 10 min static test (21°C) performed on one set of membranes. The dramatic improvement in performance (more than a doubling of flux) is evident from the figure.

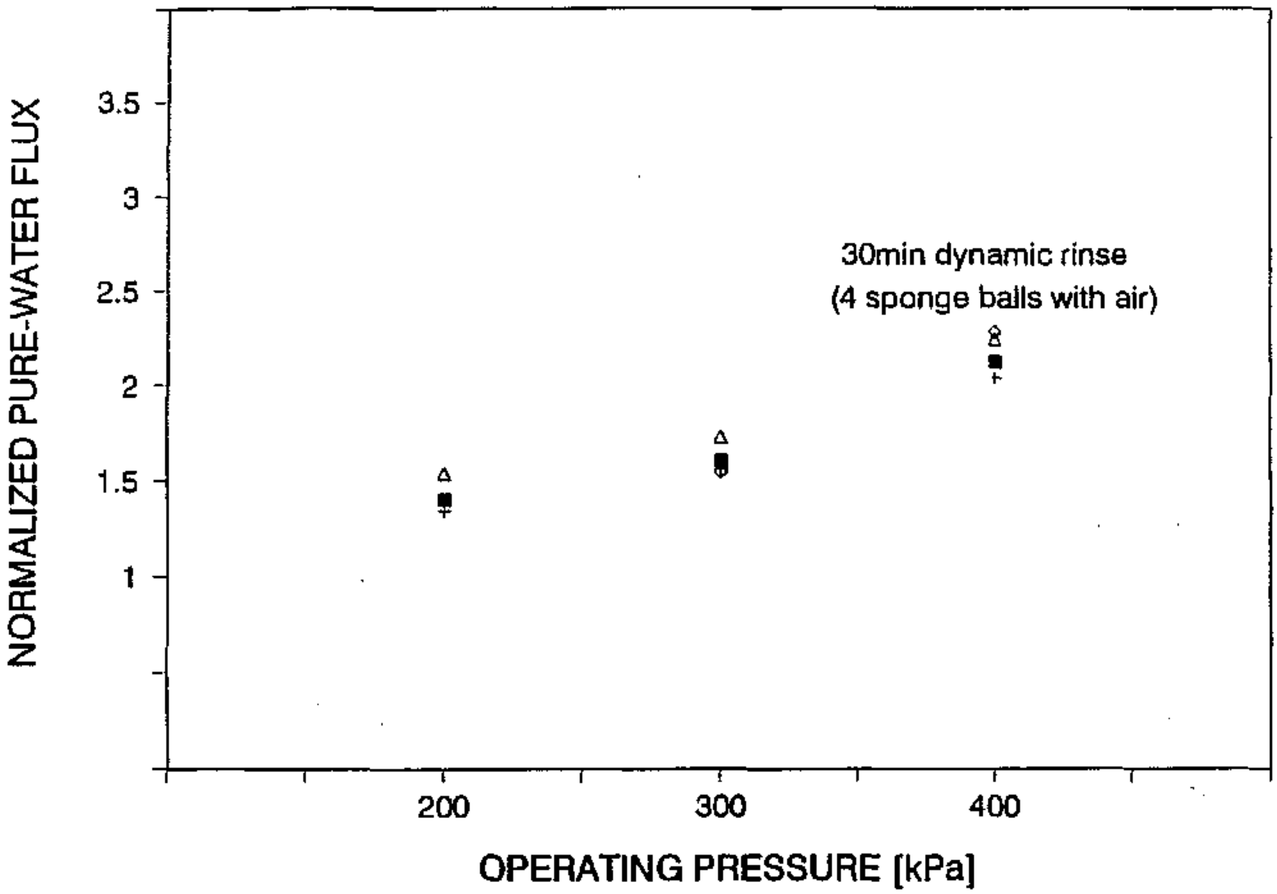


Fig. 6.5:
PWF of fouled membranes after enzyme treatment.

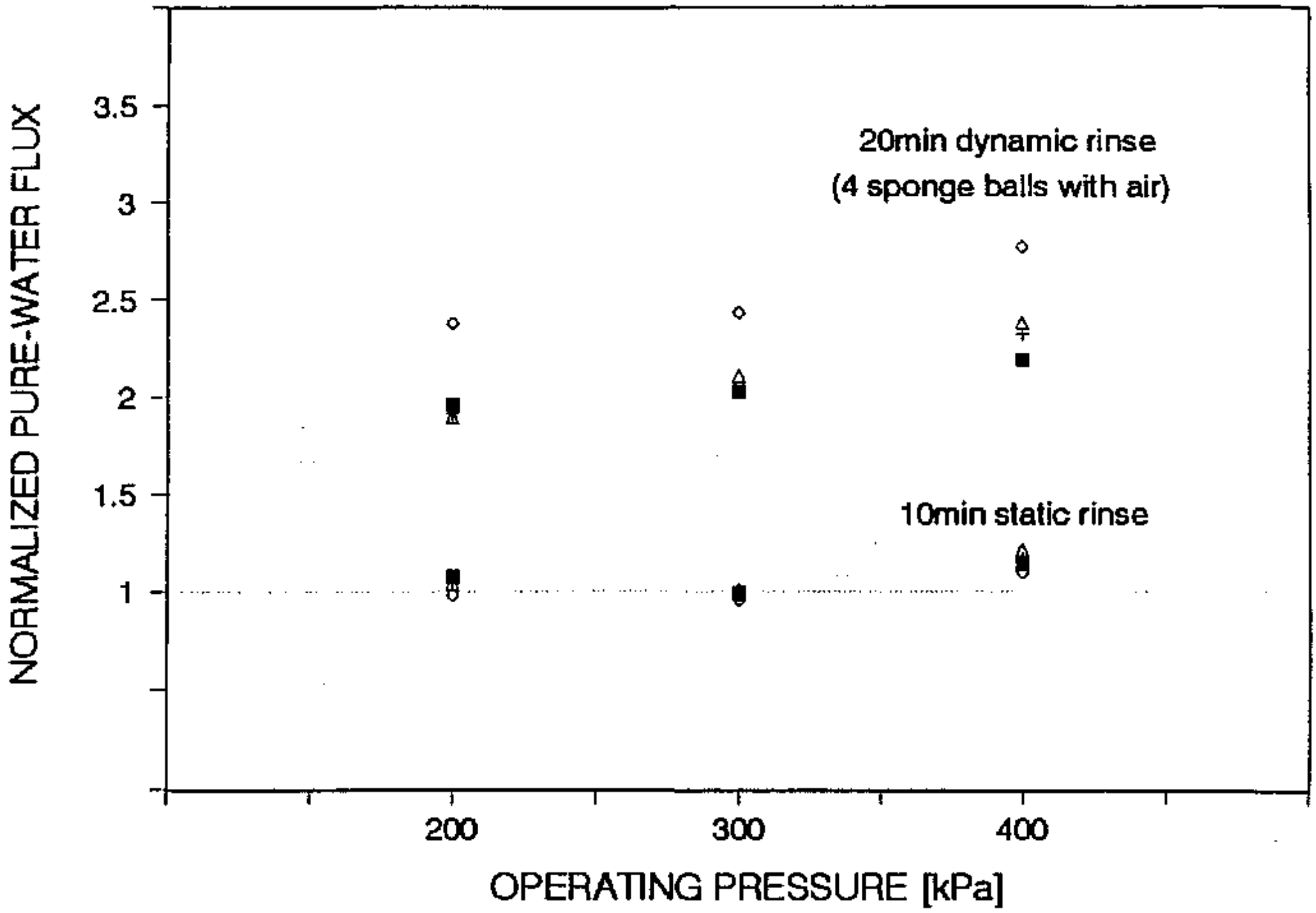


Fig. 6.6:
The role of chlor-alkali treatment in PWF restoration.

In Figure 6.7 the results of a combination of treatments are compared. Here the membranes were first subjected to a 30 min enzyme/synergizer and sponge-ball rinse. The pure-water flux was then determined. The membranes were then subjected to a 10 min chloralkali rinse, followed by another sponge-ball rinse. The pure-water flux was again determined. A remarkable three-fold, and higher, improvement in flux performance was recorded.

The summary shown in Figure 6.8 reveals to what extent flux restoration was possible. Upon removal of the membranes, and on closer inspection of the internal and external surfaces of the membrane-tube, the membranes themselves appeared shiny and clean, although the substrate still had the original slight-yellow colour.

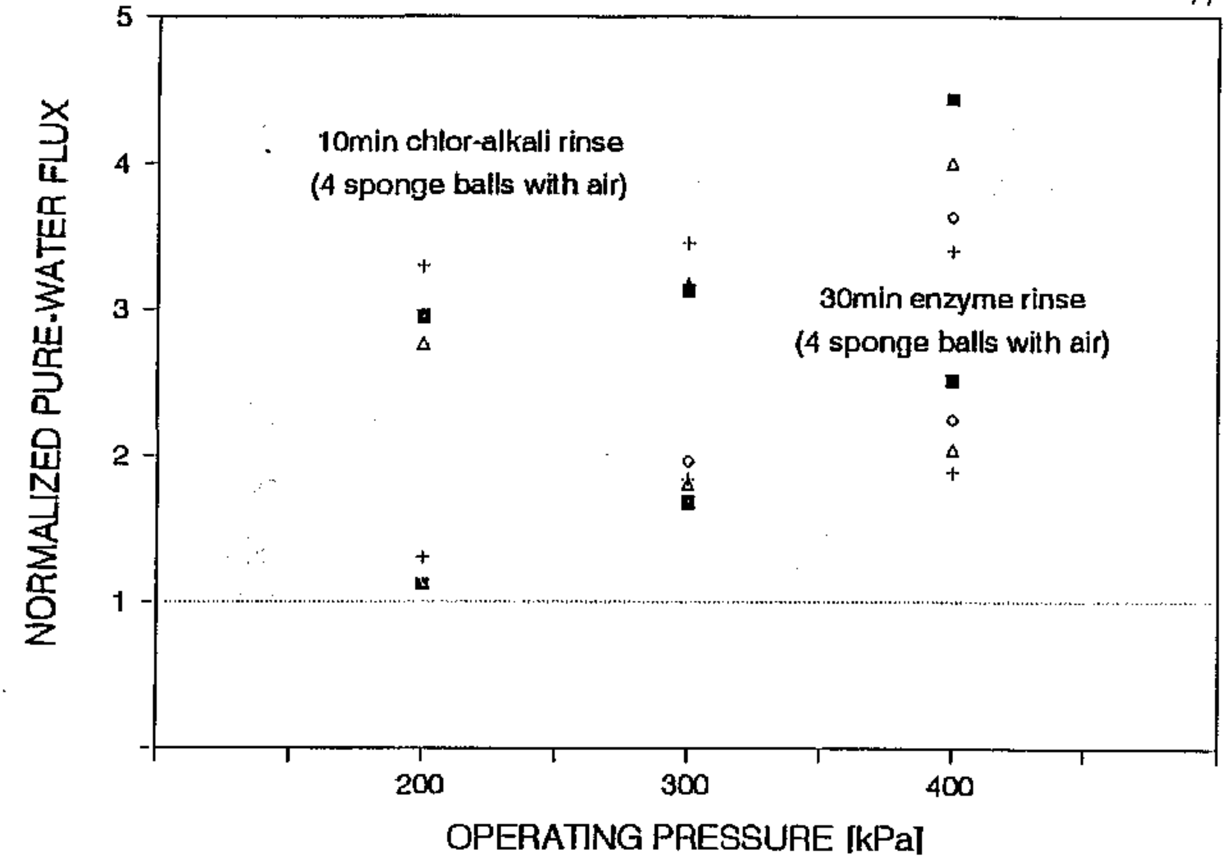


Fig. 6.7:
Effect of a combination of enzyme and chlor-alkali treatment on PWF restoration.

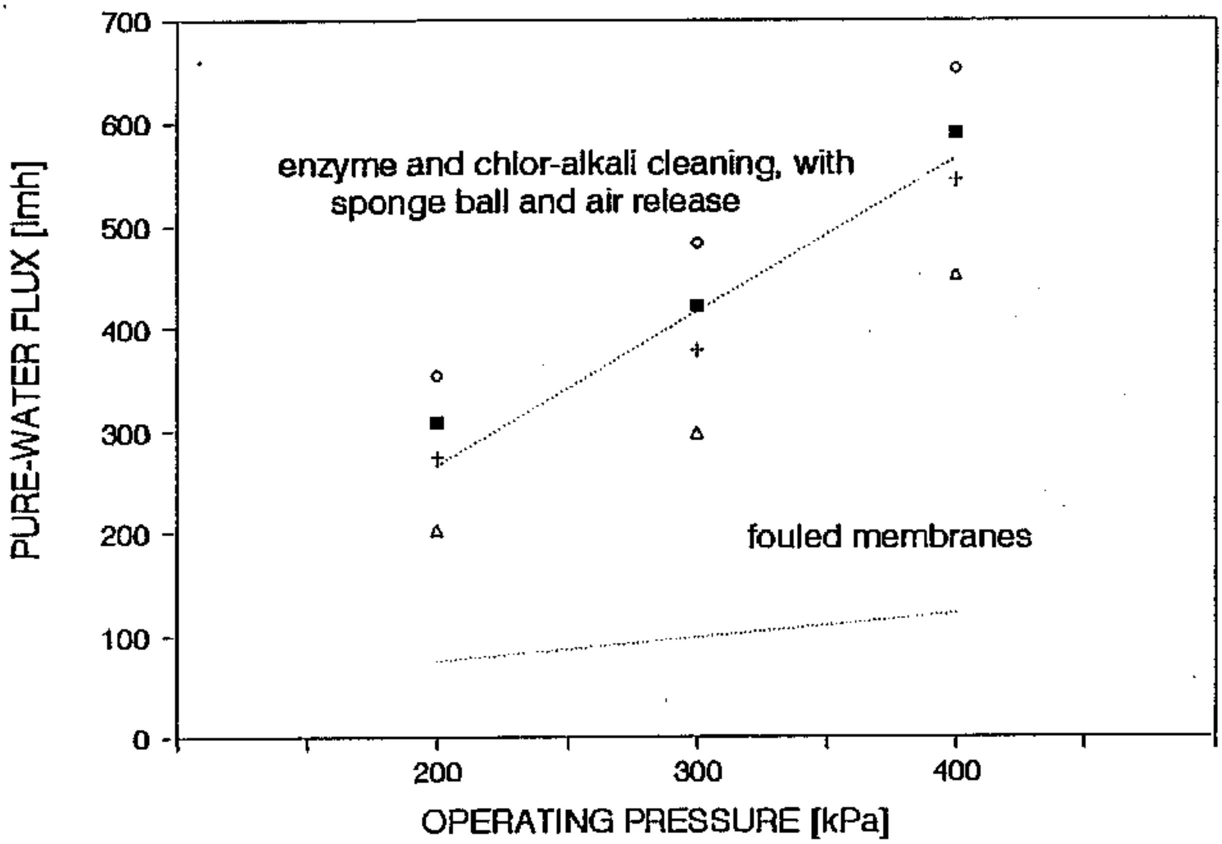


Fig. 6.8:
Effects of cleaning on performance of fouled membranes.

6.2.5 CONCLUSIONS

The short laboratory study conducted on membranes that had been obtained from the operating plant at the Cato Ridge Abattoir revealed:

1. there are indications that fats are present on the surface of the membranes;
2. indications are also that proteins have been allowed to coagulate inside the system, possibly due to interrupted operation with process fluid remaining within the membrane tubes;
3. low-temperature rinsing with cleaning solutions is not as effective as medium-temperature (about 50°C) operations;
4. proteolytic enzyme cleaners, especially those which have been developed and designed for use in the abattoir industry, are effective in breaking up the foulant deposits;
5. sponge balls are very effective in removing the loosened protein deposits by a scouring action; particularly if air is introduced to increase turbulence;
6. peptizing agents, such as chloroalkalis, are effective in bringing about an improvement in membrane pure-water flux performance;
7. it is more beneficial to membrane flux restoration if a proteolytic enzyme-cleaner rinse is followed by a chloralkali rinse; and
8. the average melting-point of the fatty deposits on the membrane surface appears to be about 51°C.

Laboratory evaluation of cleaning regimes and materials can supply valuable information when pilot-plant operations are under evaluation.

This work, in conjunction with work done by the PRG Group, Natal University, resulted in the appearance of publications in Water SA [Ref. 6.4] and several conference presentations [Refs. 6.5 and 6.6]. It has also spurred research programmes into the use of biological techniques for membrane cleaning (e.g. at the Department of Biochemistry, U.S.).

6.3 AN INVESTIGATION INTO UF MEMBRANE SYSTEMS IN SEAWATER PRETREATMENT FOR RO DESALINATION

6.3.1 INTRODUCTION

An investigation was to be carried out into the use of UF treatment as a pretreatment to seawater RO demineralization.

The use of membrane filtration, in particular UF, in the pretreatment of seawater which is to be desalinated by RO, was shown to be competitive with combined media and carbon filtration [Ref. 6.7]. Previous work on the pretreatment of seawater by UF, showed the main advantage to be the delivery of RO feedwater of sufficient quality for direct use with compact and highly efficient membrane desalinating permeators such as the hollow fine-fibre systems [Ref. 6.8]. The quality of the UF permeate was excellent and was insensitive to variations in the quality of the raw seawater intake.

The seawater on the Atlantic coast of South Africa is known for its high content of foulant materials, for example, nutrients, suspended solids and organics. These conditions have been shown to constitute major pretreatment problems during RO desalination trials near Swakopmund, Namibia [Ref. 6.9]. Membrane filtration was considered to be a viable alternative to conventional pretreatment methods, provided that operation can be kept simple and preferably automated. The development of low-cost tubular SWUF (seawater ultrafiltration) modules at Membratek and capillary ultrafiltration modules at the Institute for Polymer Science (IPS), therefore, aroused interest with regard to this application.

6.3.2 OBJECTIVES

The use of low-cost tubular and capillary PES UF modules for the pretreatment of seawater for RO desalination was to be investigated.

Mechanical and chemical cleaning regimes were to be evaluated for the restoration of the productivity of fouled membranes.

6.3.3 EXPERIMENTAL

6.3.3.1 Membrane systems

Several membrane systems were evaluated, ranging from Membratek's tubular MEMTUF^R and SWUF^R formats to IPS prototype capillary membrane modules.

The MEMTUF^R and SWUF^R systems make use of unsupported tubular UF membranes, respectively, with diameters of 9 and 13 mm. A MEMTUF^R tube bundle comprises 40 tubes which can be internally manifolded in various series-parallel flowpaths, for example, 1 x 40, 2 x 20 or 4 x 10, according to the hydrodynamic requirements of the application. Modules are manufactured in lengths of up to 3,2 m and effective membrane areas of up to 3 m². Such modules are suspended either horizontally or vertically inside a container which serves to protect the modules against mechanical damage and simultaneously acts as a permeate collection vessel. The MEMTUF^R module used in the experiment had a membrane area of 0,4 m² and a flowpath configuration of 2 x 20.

SWUF^R modules, on the other hand, consist of 26 series-connected tubes which are housed inside a 3,2 m-long uPVC tube, with a membrane area of 3 m² per module.

The well-defined flowpath of the SWUF^R module allows mechanical cleaning of the UF membrane surface with sponge balls. In both types of modules the membrane-ends and their interconnecting caps are cast into epoxy which serves to anchor the tube bundle and provides a barrier between the feed or retentate and permeate streams.

Capillary modules used in the experiment had membranes with typical external and internal diameters of 1,8 and 1,5 mm respectively. Bundles of 200 to 250 capillaries were housed in clear uPVC tubes to give an overall module length of 1 m. The internally-skinned membranes were end-potted in a tube-and-shell arrangement with a special epoxy which adheres well to uPVC.

The 719-series UF membranes used in the MEMTUF^R modules had a MMCO of 40 000 dalton while two types were used in SWUF^R modules, a similar 719-series 40 000 MMCO membrane and a 6 000 MMCO 442-series membrane. The membranes of the capillary modules had an effective MMCO of 4 000 when tested against an aqueous solution of PEG.

6.3.3.2 Operation

The various membrane systems were mounted on a suitable skid which allowed simultaneous evaluation of the different configurations. The test equipment was installed on the jetty of a fish-processing company where seawater could be obtained from existing intake piping. The raw seawater was first screened to 300 μm before being subjected to dual-media filtration. Filtered seawater was collected in a 200 l buffer tank from which it was distributed to the various modules by means of a centrifugal pump and ring manifold. Take-off points for the individual modules were provided with pressure gauges for the determination of operating pressure. The experimental set-up is illustrated schematically in Figure 6.9. A second 200 μm screen was installed ahead of the capillary module to prevent physical blocking of the capillaries by solids (e.g. carry-over grit from the sand-filter). The SWUF^R modules were fitted with a flow-reversal system for sponge ball cleaning. The flow-reversal system consisted of a Wheatstone-bridge-type arrangement of four valves, mechanically linked and actuated by a pneumatic cylinder which was fitted with an air solenoid valve and timer. Each SWUF^R module was provided with a sponge ball trap on both the inlet and outlet ends.

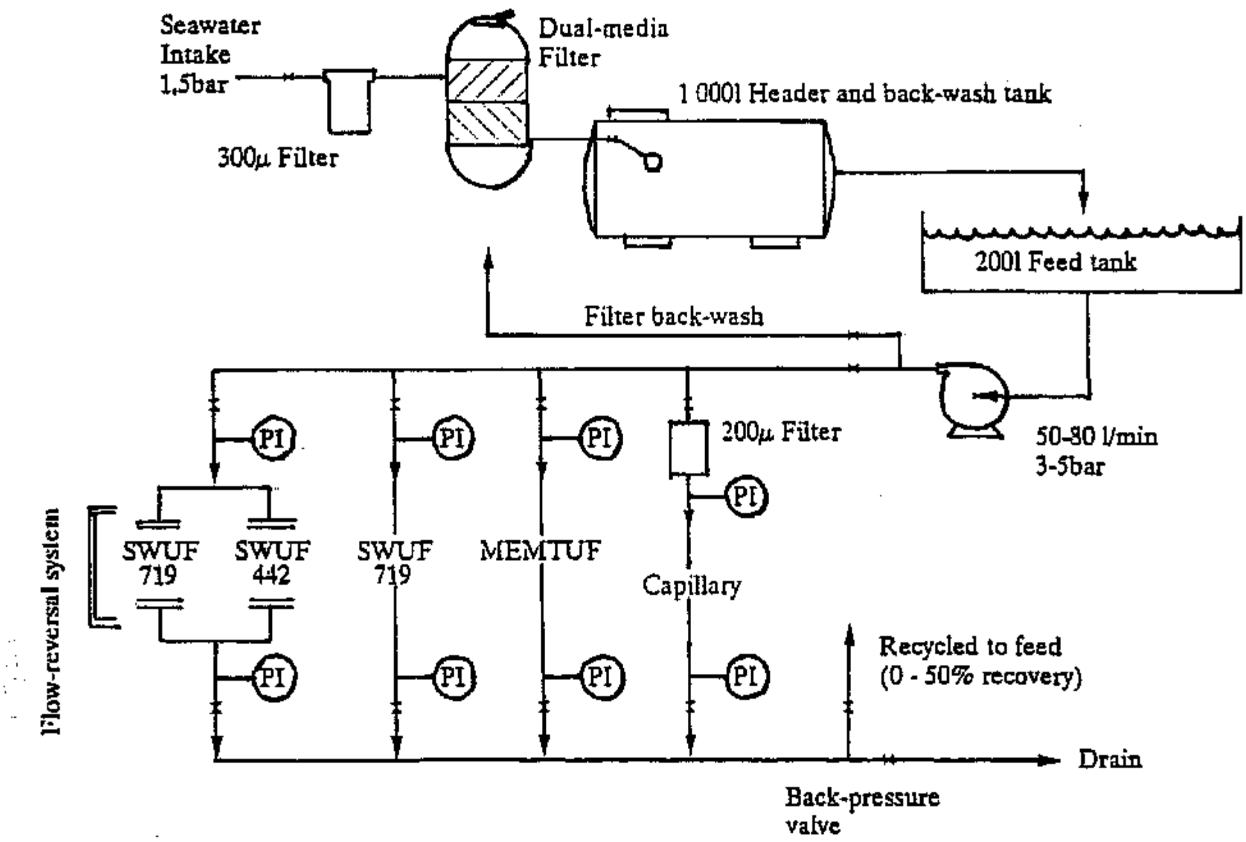


Fig. 6.9:
Schematic diagram of experimental equipment used for seawater pretreatment.

6.3.4 RESULTS AND DISCUSSION

6.3.4.1 Flux values

A. Operation with sponge balls

Mechanical cleaning of the tubular SWUF^{R} modules, with the aid of sponge balls and a flow-reversal system, proved to be effective in removing substantial amounts of foulant material. The beneficial effect of sponge ball cleaning is illustrated by the higher seawater flux values which could be maintained. For the SWUF^{R} 719 module these were found to be higher by factors of 2,4 to 6,5 (refer Fig. 6.10), when compared with operation without sponge balls. The degree to which the flux could be restored and maintained, was determined by the frequency of sponge ball cleaning. Shorter sponge ball cycle times yielded better results (Fig. 6.10), and a flow-reversal frequency of 5 min was finally adopted. A combination of sponge ball and mild chemical cleaning served to maintain seawater flux values in the region 14 to 127 lmh with an average of 74 lmh for the 1 600 h test period (refer Fig. 6.11). Frequent replacement (optimum at 100 to 200 h) of the sponge balls was required in order to capitalize on their cleaning efficiency. The flux decline associated with wear on the sponge balls, and subsequent improvement after replacement, can be clearly seen from Figure 6.11.

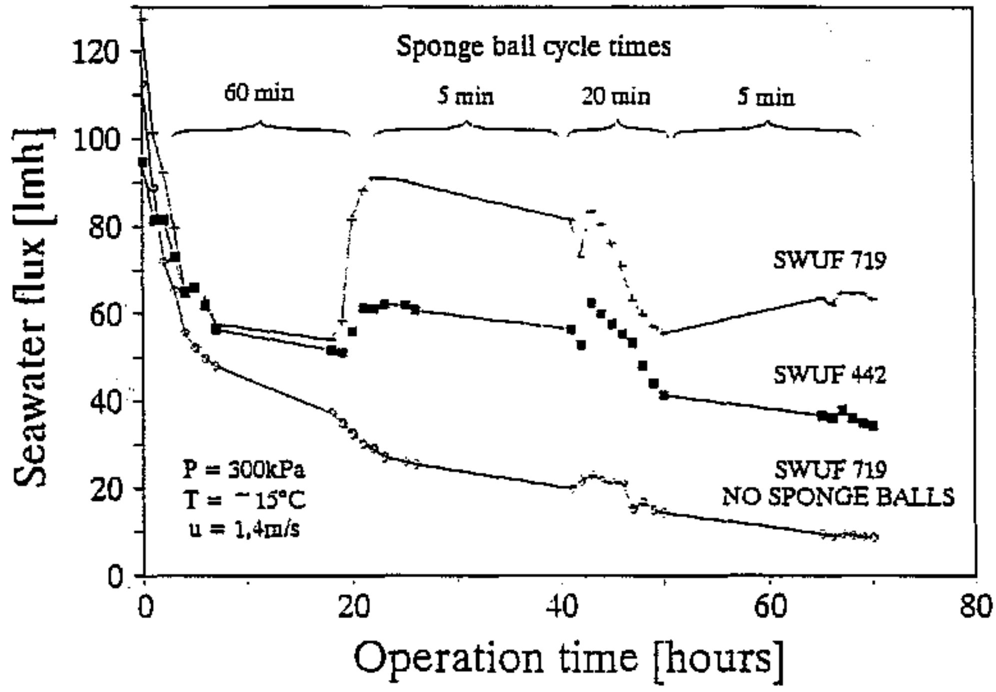


Fig. 6.10:
Effect of sponge ball cleaning on seawater flux of SWUF^R modules.

B. Operation without sponge balls

The capillary and MEMTUF^R modules, which could not be subjected to sponge ball cleaning, showed a rapid flux decline within the first 100 h of operation as illustrated in Figure 6.12. Fortunately, for the remainder of the 1 600 h test period, the seawater flux stabilized at average values of 20 lmh and 16 lmh for the capillary and MEMTUF^R modules, respectively. Since these modules were operated in parallel with the SWUF^R modules, they were subjected to identical feedwater quality and chemical cleaning cycles. The efficiency of mechanical cleaning with sponge balls is therefore apparent when the flux values for the different modules are compared (see Figs. 6.11 and 6.12).

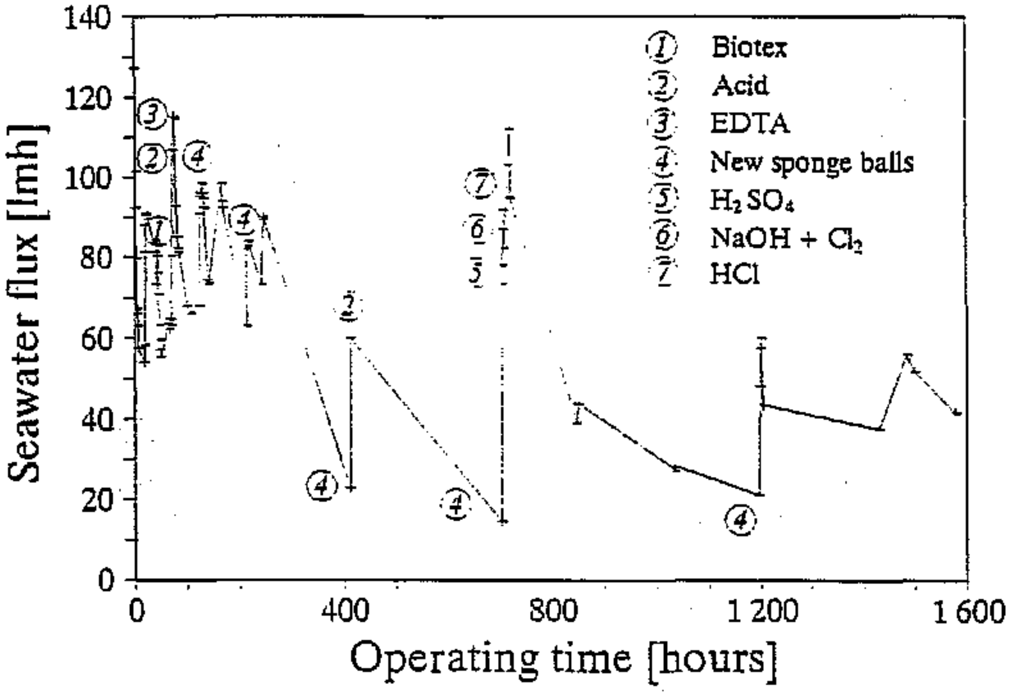


Fig. 6.11:
Plot of seawater flux against operating time for SWUF^R module (with sponge ball cleaning).

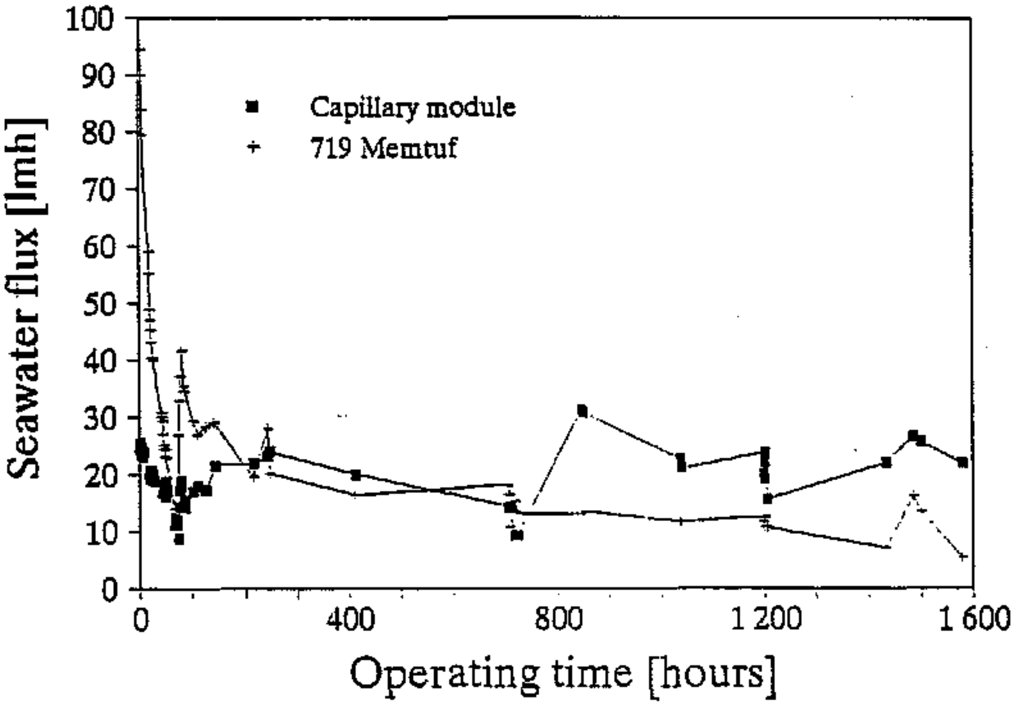


Fig. 6.12:
Plot of seawater flux against operating time for capillary and MEMTUF^R modules (no sponge ball cleaning).

6.3.4.2 Chemical cleaning experiments

Membrane samples from the SWUF^R module, which had been operating without sponge ball cleaning, were subjected to various cleaning regimes in an effort to restore the pure-water flux to its original value. The first experiment entailed the use of a combination of proteolytic enzymatic cleaners, chloralkali solution and sponge balls. These cleaning agents were found to be effective in the removal of foulants from membranes used to treat abattoir wastewaters [Ref. 6.10].

The effects of the different cleaning operations on pure-water flux restoration of membranes fouled by the seawater constituents, are illustrated in Figure 6.13. Sponge balls were employed to remove the bulk of the foulant prior to treating proteinaceous deposits with an enzymatic cleaning solution. A second sponge ball cleaning cycle resulted in a further pure-water flux increase. A final chloralkali rinse served to restore the pure-water flux to 350 to 400 lmh, which was comparable to that of a new membrane of this type under similar test conditions. The use of an extended chloralkali wash alone, together with sponge ball cleaning, also yielded good results (Fig. 6.14), but is not considered to be a viable alternative. This was due to the hydrolysis of the polyester support tubes at high pH [Ref. 6.11] and permanent modification of the membrane porosity and structure by high dosages of chlorine [Ref. 6.12].

The effectiveness of mechanical techniques to clean membrane surfaces of rapidly forming deposit layers is not queried. Flow-reversal, sponge ball swabbing and air/clean-water scouring are all tested and proven techniques. However, these techniques cannot be used with the same effect on all tube-type configurations as the narrow (also parallel) flow passages of the MEMTUF^R and capillary modules, for example, do not lend themselves to an effective sponge ball cleaning approach. It was important to determine whether similar flux increases could be obtained with the capillary and MEMTUF^R configurations by chemical cleaning alone. If the foulants were amenable to removal by chemical means, these membrane configurations were thought to be viable alternatives to the SWUF^R technology. It follows from the pure-water flux data presented in Figure 6.15 that a combination of the proteolytic enzyme wash and extended chloralkali rinse yielded values similar to those given with sponge balls (refer Fig. 6.13). The removal of foulants by chemical cleaning alone is therefore possible, albeit required at more frequent intervals.

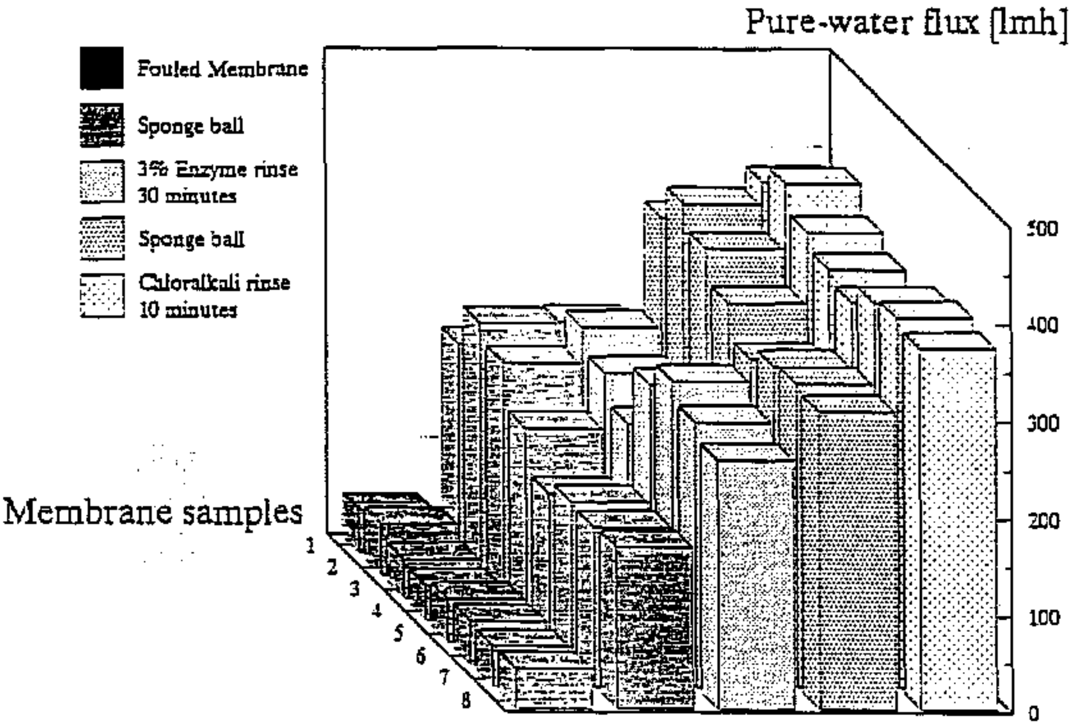


Fig. 6.13:
Effect of enzymatic, chloralkali and sponge ball cleaning-combination on pure-water flux restoration.

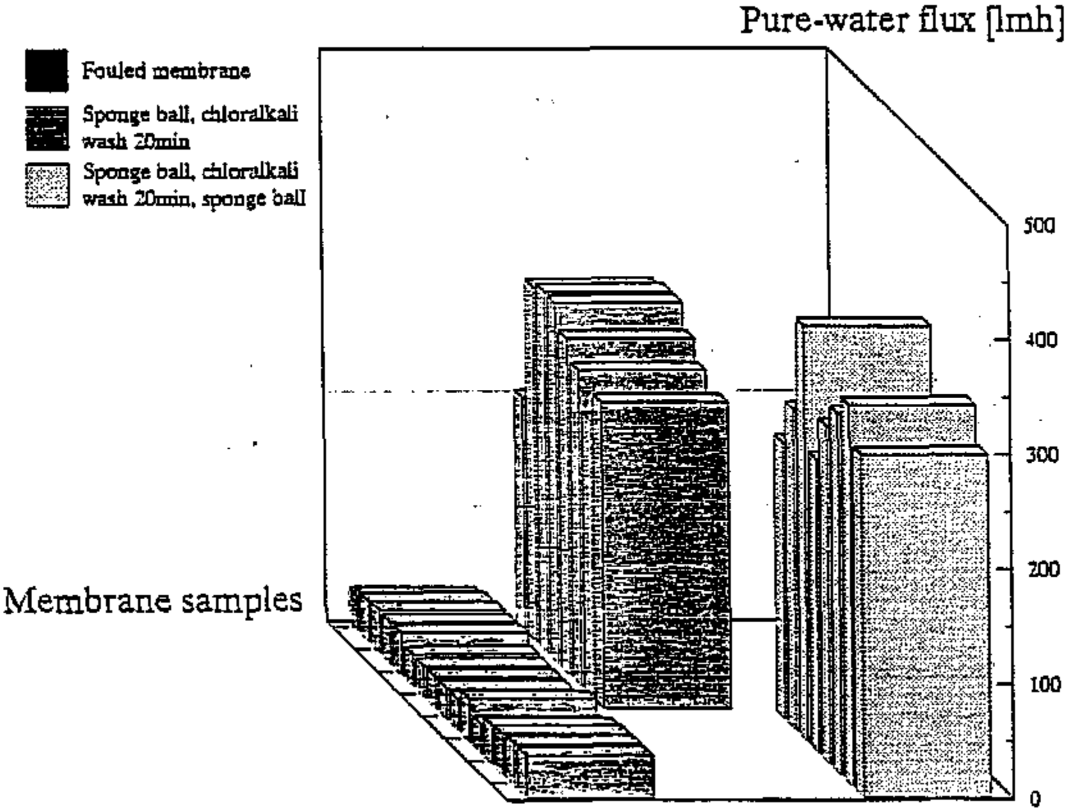


Fig. 6.14:
Effect of chloralkali and sponge ball cleaning-combination on pure-water flux restoration.

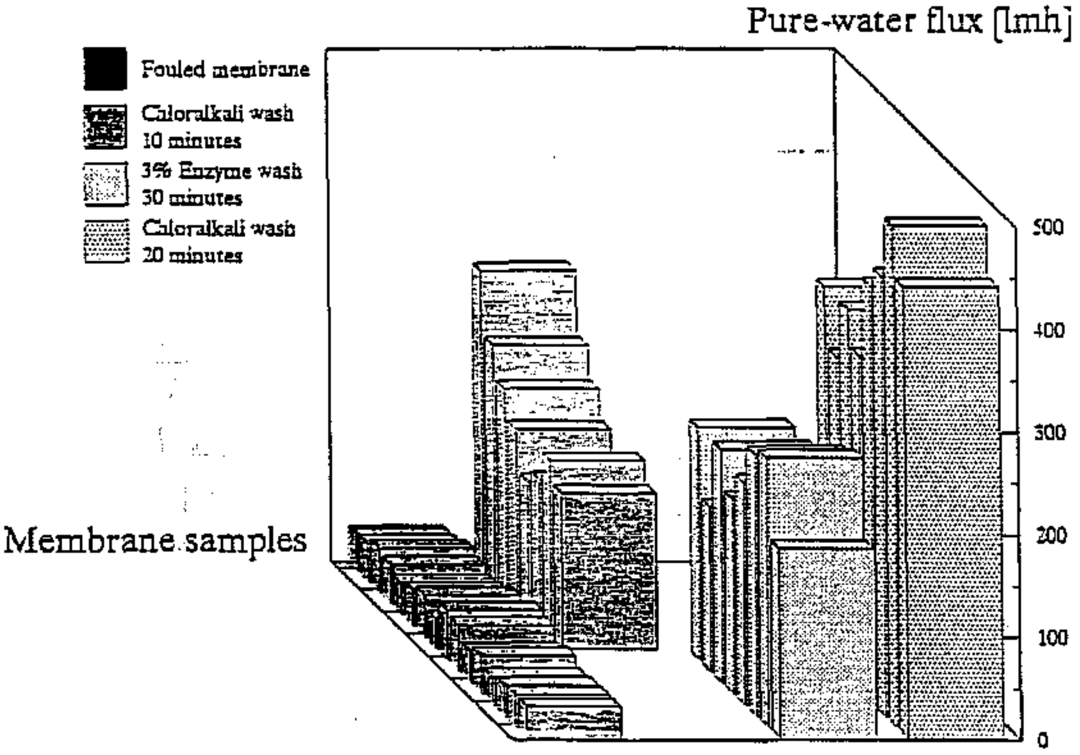


Fig. 6.15:
Effect of enzyme and chloralkali cleaning on pure-water flux restoration (no sponge ball cleaning).

6.3.4.3 Nature of foulant

Physical examination of the membrane surface indicated that the foulant comprised a gel-layer which could easily be removed by mechanical means. This explains the successful restoration of flux values by sponge ball and enzymatic cleaning. The organic fouling was thought to be compounded by inorganic and physical elements (e.g. rust, silt). Fouling can be classified as either physical, chemical or biological, and the interactive nature of fouling problems has been recognized although the complex fouling processes cannot always be readily defined [Ref. 6.13].

No significant effort was made to determine either the mechanism of the fouling that occurred, nor the nature of the gel-layers deposited on the membrane surfaces. However, EDAX analysis did indicate the presence of amounts of silica, aluminium and iron (Fig. 6.16). Subsequent cleaning with chloralkali, after enzymatic treatment to remove organics, resulted in the removal of all inorganic foulants from the membrane surface, as illustrated in Figure 6.17. The only visible emission peak on this spectrum is that of sulphur, probably originating from the membrane polymer material used.

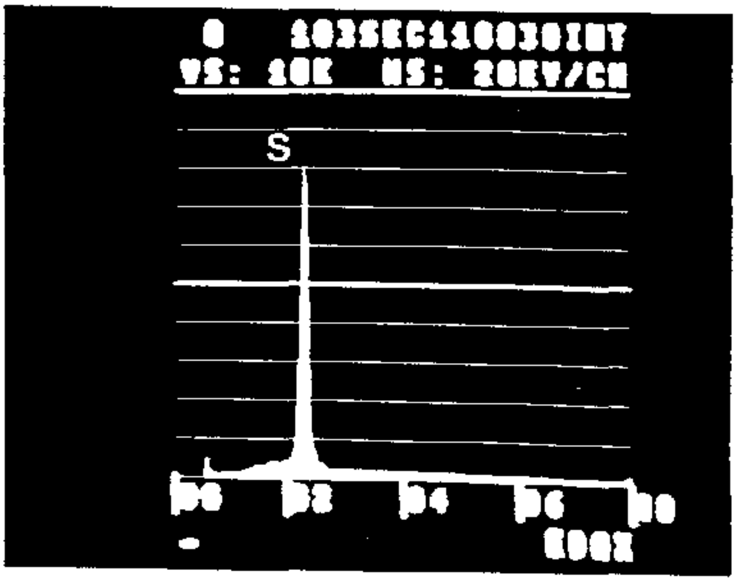


Fig. 6.16:
EDAX spectrum of fouled membrane showing various emission peaks.

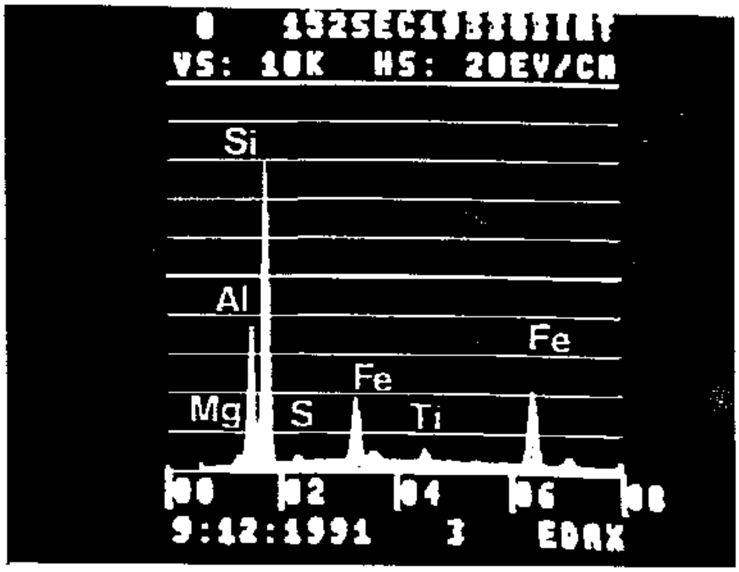


Fig. 6.17:
EDAX spectrum of membrane surface after cleaning with a proteolytic enzyme and chloralkali solution.

6.3.5 CONCLUSIONS

Medium and low cut-off UF membranes used in the pretreatment of seawater for RO remediation were found to be prone to fouling which resulted in a lowering of productivity. Tubular SWUF^R modules (13 mm tube diameter) could be cleaned mechanically with sponge balls while in operation to maintain higher average flux values. In contrast, the tubular MEMTUF^R (9 mm tube diameter) and capillary modules, which could not be cleaned by sponge balls, showed substantially lower, but stable, fluxes. The foulant could be removed by adopting a biochemical cleaning protocol with a proteolytic enzyme, followed by a chloralkali rinse.

Improvement of membrane performance will require studies of the membrane and plant operating parameters in combination with cost-effective cleaning regimes for the different geometries.

6.4 SUPPLEMENTAL POLYMER COATINGS

6.4.1 INTRODUCTION

Regeneration of CA membranes may be achieved by the treatment of substandard membranes with selected coating materials to upgrade the performance of the deteriorated or substandard membranes, thereby extending the membrane's life.

The membrane regeneration programme was re-initiated by ESKOM's requirements for the regeneration of cellulose acetate (CA) membranes operating at the RO plant at Koeberg.

However, not much has been published on this subject; a few relevant contributions are given here.

In 1971 Higley and Saltonstall of the United States [Ref. 6.14], reported that deteriorated cellulose acetate membranes were regenerated by treatment with acetic acid. These membranes were either cellulose diacetate or diacetate and triacetate blends. Damaged cellulose acetate membranes were also repaired *in-situ* by the use of colloidal guar gum solutions.

In 1973 Du Pont [Ref. 6.15], patented the use of the regeneration of semipermeable membranes by treatment with polyethers. A hollow-fibre membrane was regenerated by treatment with water containing 1% polyethylene glycol mono(alkylaminoalkyl) ether. The membrane had a water flux of 25,25 lmh and retention of 99,2% after treatment, compared to 21,6 lmh and 96,2% before treatment.

The Shibaura Electrical Company in Japan [Ref. 6.16], regenerated cellulose acetate membranes in 1977 by treating the membranes with acidic solutions containing aldehydes. Aldehydes such as formaldehyde, acetaldehyde, propionaldehyde and glyoxal were used. The retention of these membranes had decreased from 96,7% to 86,3% after 20 h of use and were restored to 97% after being treated with a solution containing 100 ml acetaldehyde, 10 ml hydrochloric acid, 2 g iron chloride and 500 ml water.

In South Africa, early regeneration work included research by H.S. Pienaar *et al.* [Refs. 6.17 and 6.18 (1978)], who treated cellulose acetate membranes with copolymers, for example vinyl acetate copolymers, to improve the membrane performance. When vinyl acetate copolymer and maleic anhydride-methylvinylether copolymer coatings were applied on spent cellulose acetate desalination membranes, salt retention properties were improved but were accompanied by a decrease in flux. The polymers were applied as aqueous solutions and insolubilized by lowering the pH to effect crosslinking.

The Toyobo Company in Japan [Refs. 6.19 - 6.22], is currently one of the companies that are actively involved in CA membrane regeneration as well as the upgrading of inferior membranes. In 1980 they patented the treatment of membranes with polyvinylpyrrolidone as a method to increase the retention of these membranes. The water permeation rate and salt retention improved to 242 lmd and 97,5% from 250 lmd and 90,5% without the PVP treatment.

In 1982 and 1983 two patents described the treatment of spent membranes with resorcinol and resorcinol-formaldehyde resins. The first patent described the treatment of spent CA membranes with 0,001% to 10% aqueous solutions of a phenolic resin to restore the membrane performances. Thus, a hollow fibre with 97,5% salt retention was treated for 2 h at 40°C by circulating a 0,01% aqueous solution of the phenolic resin comprising resorcinol 10, formaldehyde 12 and NaOH 0,4 mole, to restore the membrane performance to 99,2% salt retention without affecting the water permeation rate. This retention was stable for over 500 h. The second patent involved the treatment of used cellulose triacetate hollow fibres by immersing the membranes into a 1% resorcinol solution for 16 h. The fibres were then rinsed and an improvement of 98,54% to 99,86% in salt retention was observed. Soaking in water did not improve the retention.

The Daicel Company in Japan [Ref. 6.23], patented the thermal treatment of membranes to restore the membrane performance. When the desalination efficiency of the membranes decreased from 92% to 75% the membranes were treated with hot water at 87°C. The retention of the membranes increased to 91%.

The Development Center for Seawater Desalination in China [Ref. 6.24], stated that various reagents could be used for the regeneration of spent CA membranes. These included the use of carboxy methyl cellulose (CMC), poly(acrylic acid), modified poly(vinyl acetate) and tannic acid.

6.4.2 OBJECTIVES

The main objective of this study was to obtain a suitable method to regenerate deteriorated CA membranes by coating these membranes with a polymer material to an acceptable standard. Suitable coating materials and methods to apply such coatings were investigated. Coated membranes were evaluated for RO their performance.

6.4.3 EXPERIMENTAL

6.4.3.1 Resorcinol-formaldehyde coatings

Different resorcinol-formaldehyde resins were prepared with ratios of formaldehyde to resorcinol varying between 0,3:1 and 1,2:1. Coatings were applied to both CA RO and CA nanofiltration (NF) membranes using two different techniques: (i) a 50 ppm resin solution was circulated through the membranes at elevated temperatures and high pressures (*in-situ* coating) or (ii) the coatings were applied by dipping the membranes into a 1% aqueous solution of resorcinol-formaldehyde for 16 h at room temperature. The membranes were then tested with a 2 000 ppm NaCl-solution at 3 MPa operating pressure.

6.4.3.2 Tannic acid treatment

Membranes were first subjected to a 100 ppm PVME solution at a low pH. The initial pH-value was 4 and the pH was increased by 0,5 units every 20 min up to a final value of 6,5. Membranes were then treated with a 50 ppm tannic acid solution at pH 3,5, which was increased to a final value of 6,5 by increasing the pH by 0,5 units every 10 min. The treated membranes were then evaluated with a 1 000 ppm $CuCl_2$/2 000 ppm NaCl feed solution for 30 h.

6.4.3.3 Poly(acrylic acid) treatment

Membranes were initially subjected to a 50 ppm poly(acrylic acid) feed solution adjusted to a pH-value of 2 with H_2SO_4. The pH was then gradually increased to a value of 6,5 over a 2 h-period by addition of NaOH. The pH of the solution was then lowered to 3,5 and a 50 ppm PEG 35 000 solution was added to the feed stream. The pH was then again gradually increased to a final value of 6,5.

6.4.4 RESULTS AND DISCUSSION

6.4.4.1 Resorcinol/formaldehyde coatings

Both experimental methods 1 (circulation coating) and 2 (dip coating) improved the CA RO membranes performance to some extent. Examples of results can be seen in Table 6.3 and Figures 6.18 and 6.19.

Table 6.3: RO performances of formaldehyde/resorcinol coated and uncoated CA membranes

Formaldehyde : Resorcinol Ratio	Retention (%)		Flux (lmh)	
	Before	After	Before	After
0,45 : 1	62,26	80,90	45,74	30,33
	74,58	94,58	50,03	30,26
	84,78	95,26	32,23	25,20
0,52 : 1	60,08	91,44	58,23	33,56
	62,35	91,63	52,30	30,73
	73,08	90,40	41,37	32,90
1,20 : 1	78,42	91,00	43,45	27,83

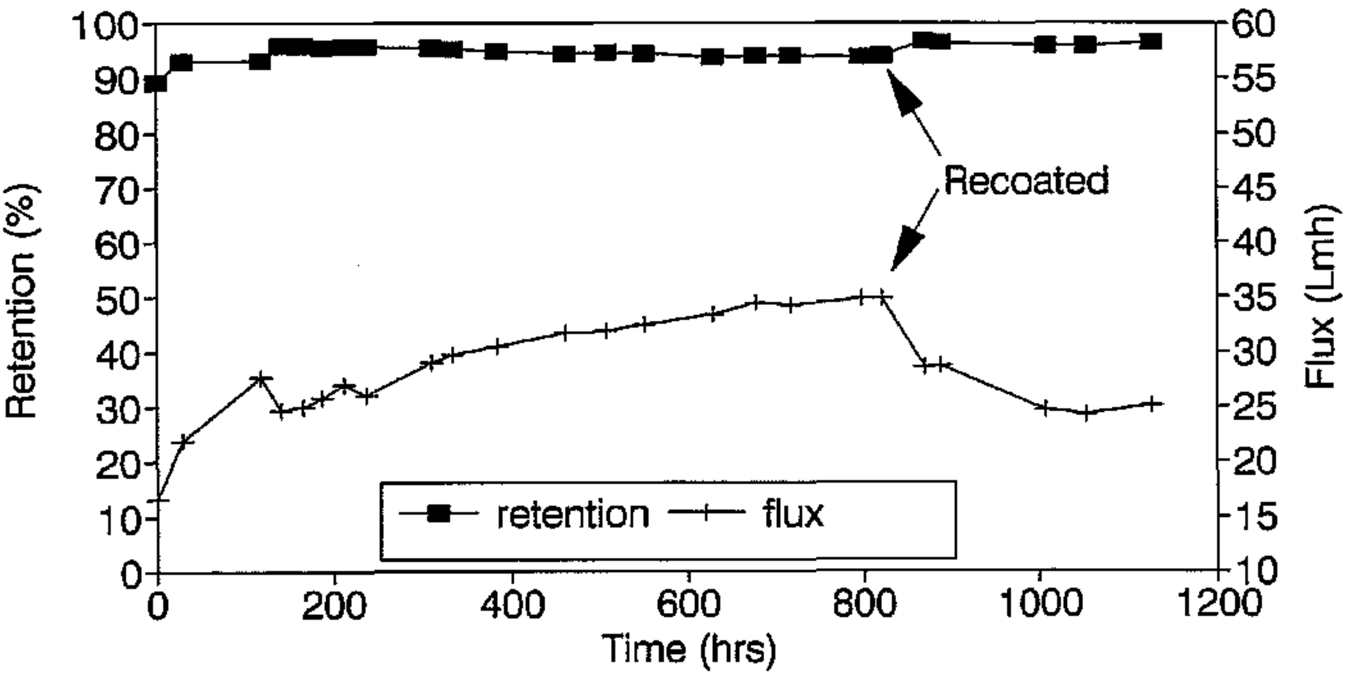


Fig. 6.18:
RO performance of resorcinol/formaldehyde coated CA membranes, coated by the dip-coating method. (First RO performance reading taken after coating.)

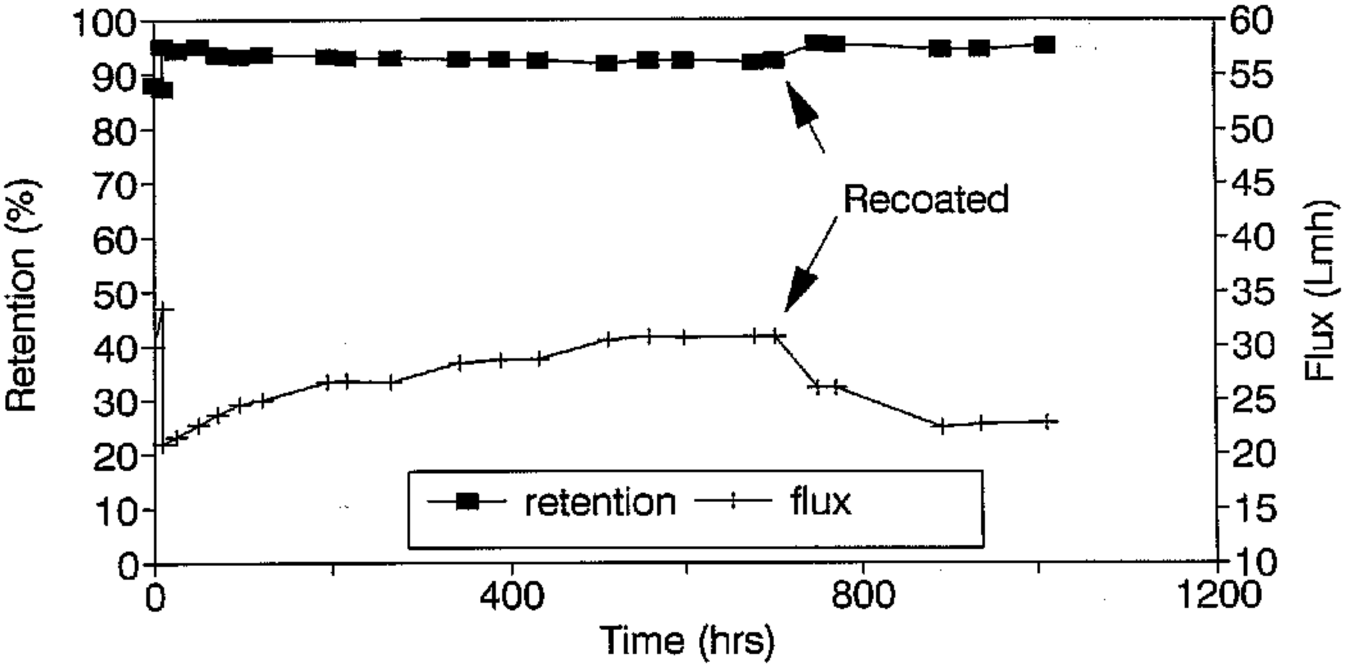


Fig. 6.19:
RO performance of resorcinol/formaldehyde coated CA membranes, coated by the circulation coating method. (First RO performance reading taken prior to coating.)

The retention performance of some membranes improved from values as low as 60 to 65% to values beyond 90%.

Higher molecular mass resins were more effective in regenerating membranes with retention values ranging from 60 to 80%, whereas lower molecular mass resins were more effective in regenerating membranes which had retention values between 80% and 90%. Decreases in flux values accompanied increases in retention; the former were also dependant on the state of deterioration of the membranes.

Several coating-layers could be applied in succession.

It was observed that membranes which had retention values of 88,9% could be improved to 96,3% by using two regenerations. The latter final values were maintained for a total test time of 350 h.

Initial tests performed on dip-coated tubular NF membranes showed an interesting development when the salt permeability and water permeability coefficients of the membranes were mapped on a log-log scale (see Fig. 6.20). The membrane performance first improved as expected (marker 30.1 to 30.2). After some time, however, a marked further improvement in the membrane performance (marker 30.3) was noticed, after which the performance started deteriorating and returned to its original state (marker 30.1). (A possible explanation is that the coating resin was being washed off, or through, the membranes surface.)

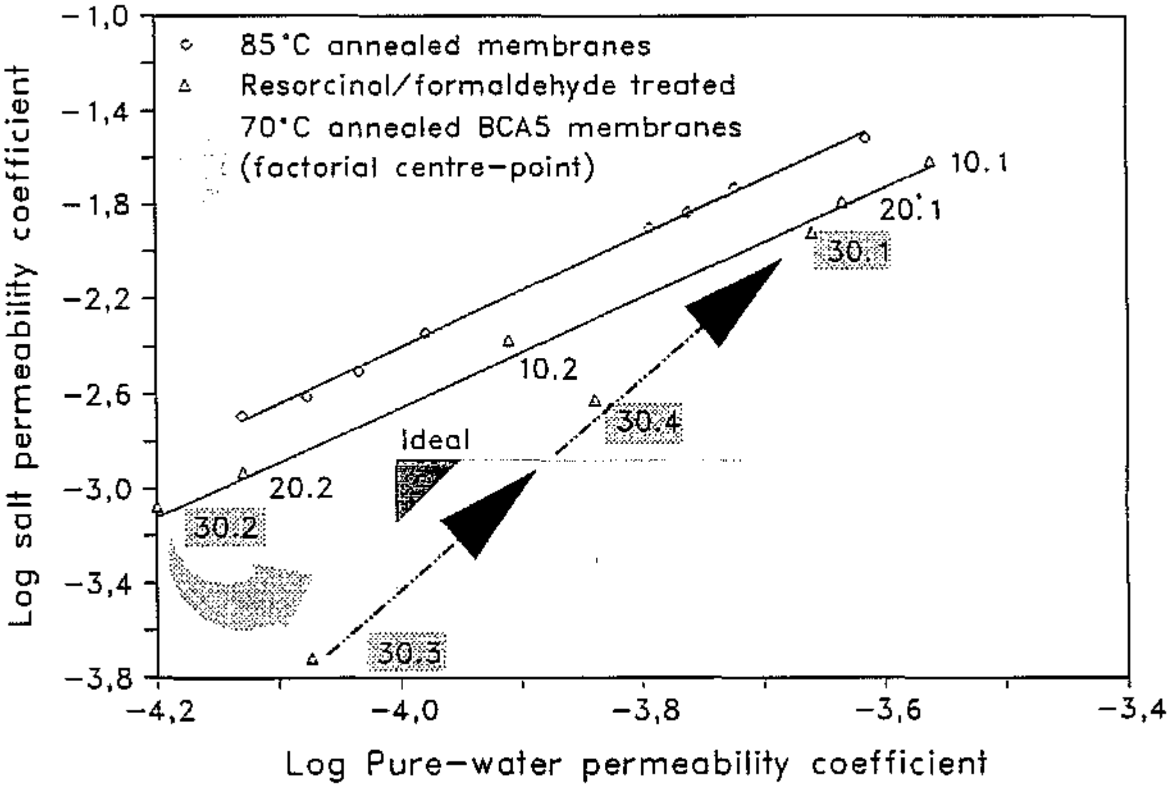


Fig. 6.20:
Resorcinol/formaldehyde-treated CA tubular NF membranes: log salt permeability vs. log pure-water permeability.

This non-linearity in performance behaviour can be an indication that the salt-retention mechanism is no longer adequately described by the capillary-flow theory in that region. This could be of great importance in the development of supplemental polymer coating materials and fixation techniques, and the explanation offered earlier may be less simple.

6.4.4.2 Tannic acid treatment

Tannic acid had a marked effect on membrane performance. The salt retention of two membranes were restored from their initial values of 73,1 and 76,2% to 90,6 and 90,7%. However, the effect of the flux performance was also marked: deteriorating from 29,1 and 25,0 lmh, respectively to 20,7 lmh. The treatment appeared stable and no further loss in performance was recorded after a 650 h test period.

6.4.4.3 Poly(acrylic acid) treatment

The RO performance of CA membranes was typically improved with tannic acid treatment, as is shown below:

Before coating:	74,6% and 43,5 lmh
After coating:	88,0% and 34,1 lmh

Although the flux of these membranes was still high enough for industrial use, the improvement in retention was considered to be insufficient.

A summary of results, comparing the effects of the various coatings on CA membranes, is given in Figure 6.21.

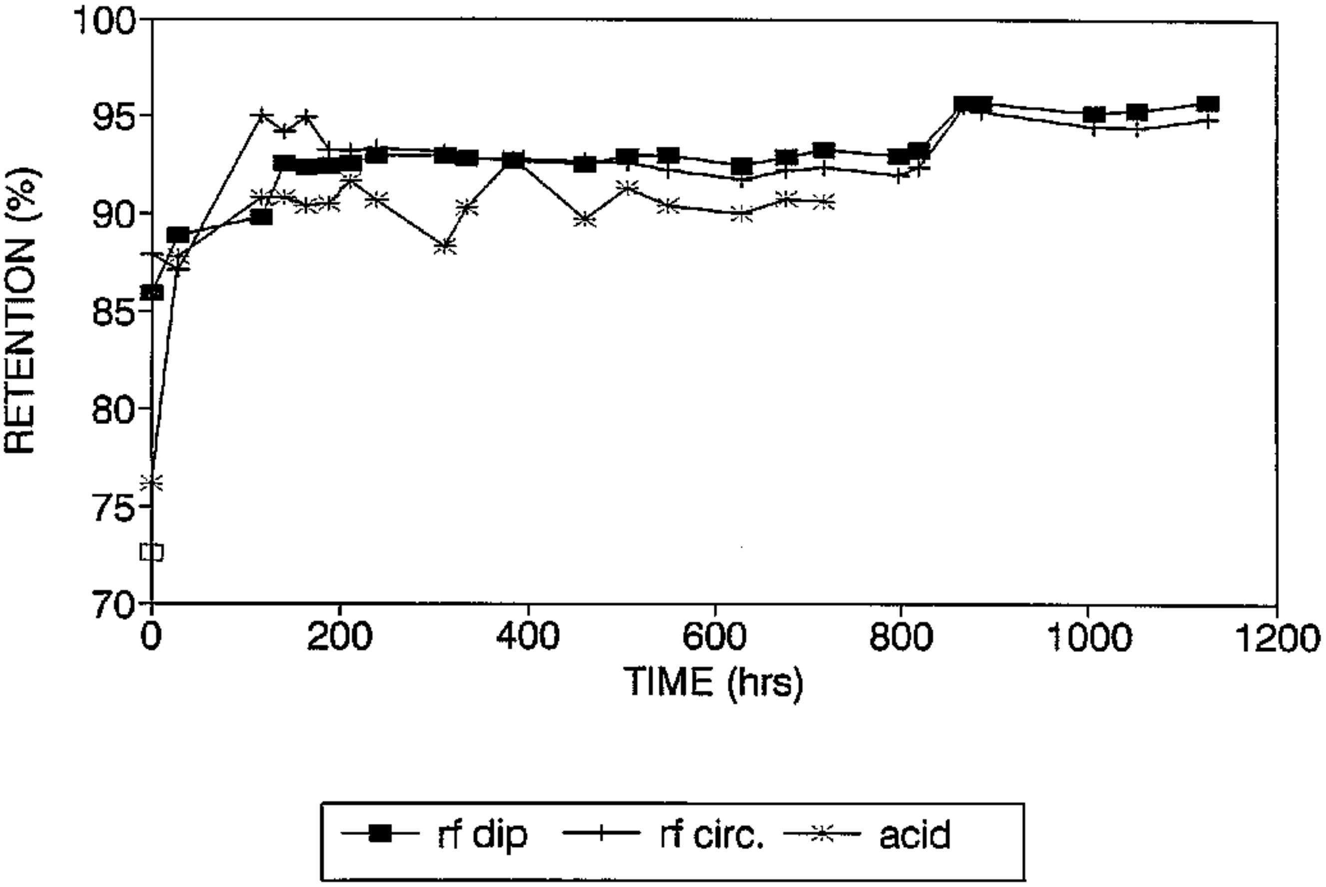


Fig. 6.21:
Comparison of RO performances of CA membranes coated in three different ways.

After comparing the RO performance of results of membranes coated by the abovementioned three different methods, it was found that the phenolic resin treatment was the most effective.

Although the other two methods, tannic acid and poly(acrylic acid) treatment, are known, inadequate results were obtained.

After comparing the different methods of applying the phenolic resin coating to the membranes, it was concluded that circulation coating (i.e. *in-situ* application) of the membranes showed more promise that the dip-coating method did. The possible reasons are: (i) the circulation coating is performed at a higher temperature than the dipcoating method, (the resins used self-cure at 40°C and a more stable coating would be created), (ii) the resins are applied at a pressure of 3 MPa which means that the resin is forced into the defects in the membrane surface. This will have to be studied further to tailormake a resin for every grade of damaged membrane. The dip-coating method only brings the resin in contact with the membrane surface, but does not allow for penetration of the resin into the membrane by force. The only way the resin can impregnate the membrane coated by this technique is by diffusion.

For industrial use *in-situ* coating will be preferable. This is especially true for coating spiral wound modules were the dipcoating method would not be as effective in effecting adequate coating of the tightly wound up membrane and force would have to be applied to ensure a uniform coating. It would also not be practical to shut down a plant for at least 16 h in order to coat the membranes by the dip-coating method. The membranes would then also have to be rinsed at high pressure to remove excess coating material and this would require more time.

Results of this work have been presented at a local conference [Ref. 6.25] and in poster form [Ref. 6.26].

6.4.5 CONCLUSIONS

Initial results have indicated the following:

1. supplemental polymer treatment improves the salt-retention performance of membranes, at the cost of reduced water flux;
2. the technique of membrane regeneration can be used to upgrade the performance of substandard membranes, or to prepare new membranes with improved properties;
3. the end-performance of the coated membranes depends on the materials with which they were coated, the coating's chemical formulation, conformation and molecular mass;

4. coatings must be tailor-made according to the pore-size distribution of the new membranes; and

5. circulation (*in-situ*) treatment with a 50 mg/l solution of a resorcinol-formaldehyde resin is an effective means of regeneration.

APPENDIX A

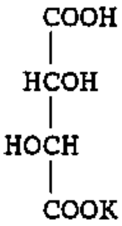
POTASSIUM BITARTRATE REMOVAL FROM WINE RESTS

A.1 CREAM OF TARTAR

Cream of tartar is also known as potassium bitartrate (KHT) and potassium acid tartrate. Grape wines contain a high concentration of potassium (0,1 to 1,2 g/l) and tartaric acid (2 to 5 g/l). Ionization of tartaric acid produces bitartrate ions which react with potassium to form the solid potassium bitartrate salt $KC_4H_5O_6^-$ (see Fig. A.1).

$$K^+ + C_4H_5O_6^- \longrightarrow KC_4H_5O_6 \qquad \text{(Eq. A.1)}$$

$KC_4H_5O_6$ Mol mass : 188,18 $g.mol^{-1}$



$$\begin{array}{c} \text{COOH} \\ | \\ \text{HCOH} \\ | \\ \text{HOCH} \\ | \\ \text{COOK} \end{array}$$

Fig. A.1:
Chemical structure of KHT.

The amount and rate of potassium bitartrate formed are controlled by the solubility product,

$$(SP) = [K^+]\,[HT^-]$$

where HT^- denotes the bitartrate anion $C_4H_5O_6^-$ which depends on temperature, pH and the ethanol content of the solution. While tartaric acid ($C_4H_6O_6$) has the characteristics of a general-purpose acid, fluctuating availability and price have caused users to re-use it where possible. Apart from a very limited synthetic production of the compound in South Africa, tartaric acid is extracted from wine lees residues.

A.2 USE OF CREAM OF TARTAR IN THE WINE INDUSTRY

Potassium acid tartrate is one of the major ingredients used in the food and wine industry. The most common tartrate present in wine is that of potassium bitartrate.

The amount of KHT crystals present in wines differs from fermentation batch to batch and from one wine to another. In most young wines the amounts of K^+ and HT^- are higher than the solubility of KHT, and therefore the KHT solution becomes supersaturated. During and after fermentation of the wine, precipitation of KHT will take place mainly because of:

(i) any decrease in temperature; and

(ii) the increase in the amount of alcohol present.

In South Africa, addition of tartaric acid to most wines is permitted, to increase their acidity. It is, however, important to stabilize these wines before bottling to prevent settling-out of tartrates in the product at low temperatures. KHT is also added to wines as a nucleating agent during certain tartrate stabilizing processes to enhance the rate of KHT precipitation.

Two of the wine stabilizing processes used in industry are:

(i) cold stabilization [Refs. A.1, A.2 and A.3]; and

(ii) the contact process [Refs. A.1, A.4 and A.5].

The former method comprises the removal of KHT by storing the wine for 2 to 14 days at temperatures 1 °C above freezing point. The latter process basically means that a predetermined quantity of KHT crystals (usually 4 g/l) is constantly in contact with the wine at the stabilization temperature for a certain period. The KHT crystals are introduced into the wine at the beginning of the treatment as a seeding agent. It is circulated by agitation of the wine, and its volume increases by the supersaturated portion of the wine treated. It thus follows that approximately 10 to 20% of the contact tartrate can be continuously removed after precipitation.

Currently, variations of the two stabilization methods mentioned above are used by wine industries. The precipitated KHT is removed continuously from treated (stabilized) wine by means of hydrocyclones, centrifuges and separators, and is added to an incoming stream of wine before the cooling-down process starts again [Refs. A.6 and A.7]. A typical system for KHT stabilization is shown in Figure A.2.

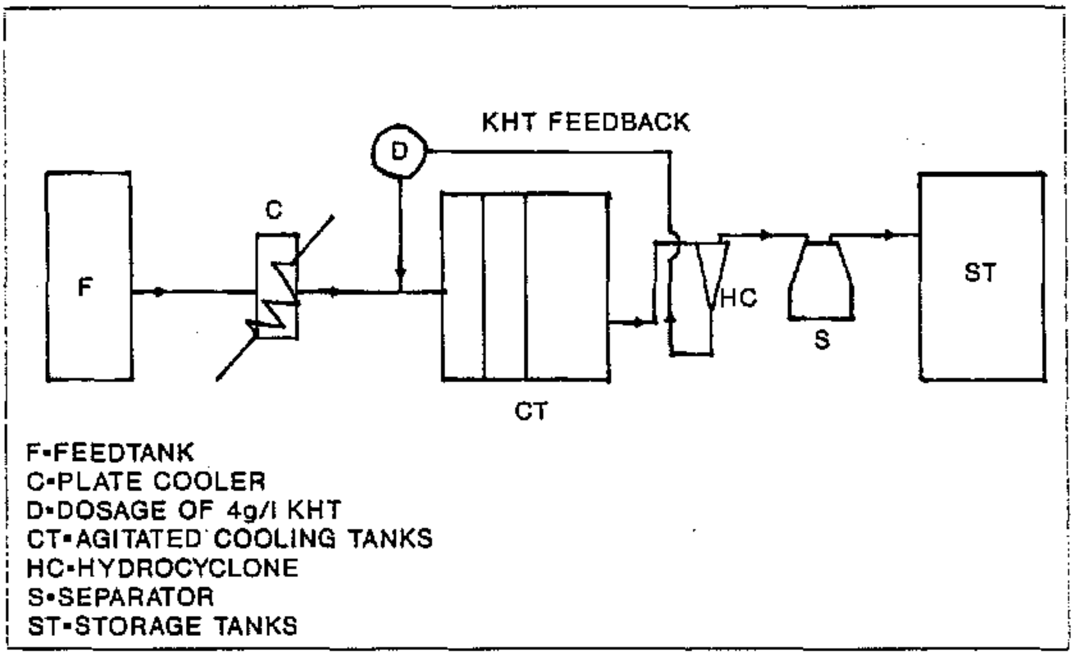


Fig. A.2:
The contact process for KHT stabilization.

A.3 PROTEIN AND YEAST CELL FRACTION OF WINE LEES

The study of the behaviour of KHT in hydro-alcoholic solutions and in wines has shown that the precipitation is slower in wines. This is because of selective adsorption of certain substances in the wines onto the faces of the crystals, which impedes crystal growth [Ref. A.8]. Wine tartrates have been found to contain 0,011 to 0,064% protein fraction.

The yeast cell and protein fraction of wine are often present as colloidal or macromolecular structures. It is this component of wine, together with impurities, that inhibits tartrate crystallization. An experiment has shown that efficient removal of most colloids with a membrane with a MMCO of 10 000 dalton resulted in an acceleration of KHT precipitation [Ref. A.9]. However, cross-flow filtration with a 0,2 μm membrane did not affect tartrate precipitation. Even small amounts of colloids were sufficient to inhibit tartrate crystallization, an effect that was also noted with protein-containing additives (e.g. casein, kieselguhr) and which barely responded to cross-flow filtration.

In another experiment conducted by Piracci [Ref. A.10] a protein-rich colloidal fraction was isolated from wine and separated on the basis of molecular mass by using, amongst other methods, ultrafiltration. Many subfractions with molecular mass of between 10 000 dalton and 1 000 000 dalton showed some capacity to inhibit the precipitation of KHT. Although high-molecular mass proteins were especially active, inhibition was also associated with components of molecular mass less than 10 000 dalton.

A large portion of wine lees consists of proteins and yeast cells [Ref. A.11]. These constituents of wine lees are bound to cause problems in the fractionation of the lees because of the affinity of KHT for proteins and yeast cells.

The methods used for KHT extraction from wine lees usually include the use of different chemical methods [Ref. A.12]. The use of a filtration method to improve separation of tartrates from the yeast cells fraction of wine lees is described by Getov *et al.* [Ref. A.13].

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