DEVELOPMENT AND APPLICATION OF ULTRAFILTRATION AND REVERSE OSMOSIS MEMBRANES

by

GIDEON FRANCOIS MALHERBE

Thesis presented in partial fulfillment of the requirements of

Master in Technology

at the

Cape Technikon

Research carried out at the University of Stellenbosch

Institute for Polymer Science

January 1993

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ABSTRACT

Various experimental and established membranes were tested on industrial effluents. Ultrafiltration, reverse osmosis and nanofiltration membranes were used in various applications. Research was done on aspects such as the cleaning of fouled membranes, production quality control and process development.

Polyvinyl alcohol ultra-thin-film reverse osmosis membranes were manufactured for the desalination of brackish water to a potable standard. The membranes were manufactured in the tubular configuration.

Experimental ultrafiltration, reverse osmosis and nanofiltration membranes were tested on cooling water blowdown on a laboratory-scale. On-site testing was done directly on the effluent at a later stage. A study was also conducted to determine the effect of gel-polarization on membrane performance. The gel-layer model was used to predict the limiting flux of specific membranes.

Membrane processes were also applied in the fractionation of wine-lees to provide usable by-products such as yeast cells and potassium bitartrate. Ultrafiltration membranes operated in diafiltration mode were used to "wash" the slurry at different solid concentrations. The bitartrate-rich permeate collected from ultrafiltration was then concentrated using reverse osmosis and nanofiltration to allow subsequent precipitation of the product.

OPSOMMING

Verskeie eksperimentele en gevestigde membrane is getoets op industriële uitvloeisels. Ultrafiltrasie, tru-osmose en nanofiltrasie membrane is in verskeie toepassings gebruik. Navorsing is gedoen oor aspekte soos die skoonmaak van bevuilde membrane, produksie van membrane en prosesontwikkeling.

Ultra-dun-film (polivinielalkohol) tru-osmose membrane is vervaardig vir ontsoutings doeleindes. Die membrane is vervaardig in buis konfigurasie.

Toetslope is gedoen op verkoelingsafblaas uitvloeisel deur gebruik te maak van eksperimentele ultrafiltrasie, tru-osmose en nanofiltrasie membrane. Die toetse het eers net op laboratorium skaal plaasgevind, maar is later direk op die uitvloeisel by die industrie gedoen. 'n Studie is ook gedoen om die invloed van gel-polarisasie op membraan werkverrigting vas te stel. Die gellaagmodel is gebruik om die grens-vloed van spesifieke membrane te bepaal.

Membraanprosesse is ook toegepas in die fraksionering van wynmoer in bruikbare produkte soos gisselle en kremetart. Ultrafiltrasie membrane is deur middel van diafiltrasie gebruik om die wynmoer/water mengsel by verskillende vastestof konsentrasies te "was". Die bitartraat-ryke permeaat wat van die ultrafiltrasie proses verkry is, is gekonsentreer deur van tru-osmose en nanofiltrasie gebruik te maak om sodoende die produk (kremetart) neer te slaan.

ACKNOWLEDGEMENTS

Grateful appreciation is expressed to the Water Research Commission, the Institute for Polymer Science and Sasol for their financial support, without which this project would not have been possible.

Special thanks to:

Ed Jacobs, dr. Sanderson and Francis Petersen for their guidance and support during the past two years.

I would also like to express sincere thanks to the following people for help and assistance rendered during my research:

Deon Bezuidenhout (IPS)
Aneli Fourie (IPS)
Charl Morkel (IPS)
Felix Lancaster (IPS)
Erinda Cooper (IPS)
Elizabeth Isaacs (IPS)
Deon Niewenhuys (Sasol)
Dup du Plessis (Sasol)

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LIST OF ABBREVIATIONS

API - AMERICAN PETROLEUM INDUSTRY
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
COD - CHEMICAL OXYGEN DEMAND
CPA - 2-CHLORO-P-PHENYLENEDIAMINE
CTE - COOLING TOWER EVAPORATION
CWB - COOLING WATER BLOWDOWN
ETP - EXCESS WATER TO PONDS
FF - FRESH FEED
Fig. - FIGURE
HC - HYDROCYCLONE
HOIPS - CODE NAME FOR EXPERIMENTAL UTF-RO MEMBRANE
HVP - HYDROLYSIS VEGETABLE PROTEIN
IAWQ - INTERNATIONAL ASSOCIATION ON WATER QUALITY
IPC - ISOPHTHALOYL CHLORIDE
IPS - INSTITUTE FOR POLYMER SCIENCE
KHT - POTASSIUM BITARTRATE
LMH - LITRES/m^2/HOUR
MF - MICROFILTRATION
MM - MOLECULAR MASS
MMCO - MOLECULAR MASS CUT-OFF
N/A - NOT AVAILABLE
NF - NANOFILTRATION
O/FLOW - OVERFLOW
PCW - PROCESS COOLING WATER
PEG - POLYETHYLENE GLYCOL
PIP - PIPERAZINE
ppm - PARTS PER MILLION
PVAM - POLYVINYLAMIDINE
PVC - POLYVINYL CHLORIDE
PVOH - POLYVINYL ALCOHOL
RCW - RECYCLED WATER
Re - REYNOLDS NUMBER (DIMENSIONLESS)
REC. - RECOVERY
Ref. - REFERENCE
RO - REVERSE OSMOSIS
RXW - REACTION WATER
SABS - SOUTH AFRICAN BUREAU OF STANDARDS
Sc - SCHMIDT NUMBER (DIMENSIONLESS)
SCL - M-SULPHONYL BENZOYL CHLORIDE
SEM - SCANNING ELECTRON MICROSCOPE

SGL	-	STRIPPED GAS LIQUOR
Sh	-	SHERWOOD NUMBER (DIMENSIONLESS)
SP	-	SOLUBILITY PRODUCT
T	-	TARTRATE
TAB	-	3,3'-4,4'-BIPHENYL-TETRAMINE
TDS	-	TOTAL DISSOLVED SOLIDS
TEA	-	TRIETHYLAMINE
TMC	-	TRIMESOYL CHLORIDE
TRO	-	TUBULAR REVERSE OSMOSIS
TSP	-	TRISODIUM ORTHOPHOSPHATE
U/FLOW	-	UNDERFLOW
UF	-	ULTRAFILTRATION
UTF	-	ULTRA-THIN FILM
WRC	-	WATER RESEARCH COMMISSION

LIST OF SYMBOLS

a	ACTIVITY	(-)
A	AREA	m^2
C	CONCENTRATION	kg/m^3
C_b	BULK CONCENTRATION	kg/m^3
C_f	FEED CONCENTRATION	kg/m^3
C_g	GEL-LAYER CONCENTRATION	kg/m^3
C_m	CONCENTRATION AT MEMBRANE SURFACE	kg/m^3
C_p	PERMEATE CONCENTRATION	kg/m^3
d	DAY	s
D	DIFFUSION COEFFICIENT	m^2/s
d_i	INSIDE DIAMETER	m
μ	VISCOSITY	Pa.s
g	GRAVITATIONAL ACCELERATION	m/s^2
h	HOUR	s
he	HEAD-LOSS DUE TO EXPANSION	m
hf	FRICTIONAL HEAD-LOSS	m
hf_{cap}	FRICTIONAL HEAD-LOSS IN CAPILLARY MEMBRANE	m
hf_{piping}	FRICTIONAL HEAD-LOSS IN PIPING SYSTEM	m
J	FLUX THROUGH MEMBRANE	m/s
J	FRESH-WATER FLUX	m/s
j	FRICTION FACTOR	(-)
J_l	LIMITING FLUX THROUGH MEMBRANE	m/s
k	MASS-TRANSFER COEFFICIENT	m/s
L	LENGTH	m
N	AMOUNT OF MEMBRANES, TUBES, ETC.	(-)
ρ	DENSITY	kg/m^3
P	HYDRAULIC PRESSURE	Pa
Q	VOLUMETRIC FLOWRATE	m^3/s
R	RESISTANCE	$m^2.s.Pa/m^3$
T	TEMPERATURE	K
t	TIME	s
ξ	PIPE ROUGHNESS	m
v	LINEAR VELOCITY	m/s
V	VOLUME	m^3
z	BOUNDARY LAYER THICKNESS	m

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 reverse osmosis are probably the earliest and best known applications.

RO is essentially a dewatering process, whereas ultrafiltration is a fractionation technique that can simultaneously concentrate macromolecules or colloidal substances in process streams. Today, UF is applied in a wide variety of fields, from the chemical industry, such as electrocoat paint recovery, latex processing and recovery of lubricating oils, to medical applications, such as hemo dialysis and filtration operations. Many UF industrial applications to date have been secondary operations, that is, in waste treatment or recovery of valuable products from plant effluents (such as cheese whey). However, the scientific and trade literature indicates a number of applications where UF is also required as a primary unit operation. Amongst them are cheese-making by ultrafiltration, and the production of vegetable protein isolates and concentrates, and biotechnology-oriented applications, such as the harvesting of microbial cells, fractionation of fermentation broths, and as high-performance membranes in bioreactors for enzymatic and fermentation processes.

The general advantages of 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 changing feed streams;
(iv) membrane systems often use less energy than conventional treatment systems;
(v) membrane systems have potentially lower capital and operating costs than conventional treatment systems [Ref. 1.2].

1.2 OBJECTIVES OF THIS STUDY

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

The objectives of this study were:

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

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

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

(iv) solving of problems associated with membrane applications, that is, cleaning methods, etc;

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

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

(vii) determination of the role of a gel-polarized layer on the membrane surface; and

(viii) fabrication of tubular UTF-RO membranes.

1.3 MEMBRANE APPLICATIONS INVESTIGATED

1.3.1 UTF RO MEMBRANES FOR BRACKWATER TREATMENT

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

1.3.2 TREATMENT OF COOLING WATER BLOWDOWN WITH MEMBRANE PROCESSES

In a closed system in industry, 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. The above problems can be combatted by bleeding a constant stream of effluent to evaporation ponds or use 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 is the most suitable for solving the specific problem?

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

It was decided to test ultrafiltration and reverse osmosis membranes on Sasol effluent. Cooling-water blowdown was selected as the most suitable stream for testing the membranes on because of the fact that 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 (Fig. 1.1).

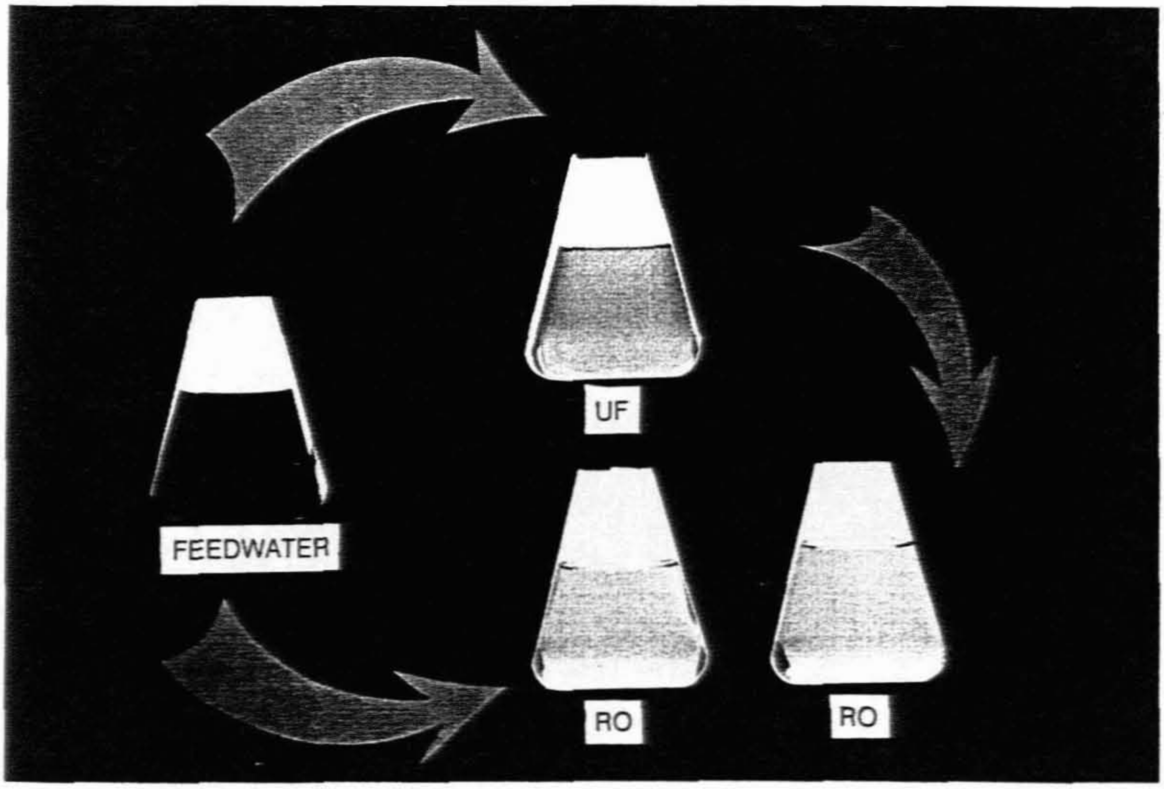


Fig. 1.1:
UF and RO on CWBD

Established membranes as well as experimental ones were tested first on a laboratory scale at the university 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 constantly work on fresh effluent in order to simulate true operating conditions during testing. After extensive testing it was decided to 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 regularly the necessary test data. Tubular UF membranes, capillary UF membranes, nanofiltration membranes and various RO membranes were thus tested on site on CWBD. This investigation supplied valuable information regarding the performance of experimental membranes and also helped with the identification and elimination of problems which arose.

1.3.3 POTASSIUM BITARTRATE RECOVERY FROM WINE RESTS WITH MEMBRANES

The main objective of this study was to determine whether membrane processes can be applied in the fractionation of wine lees to produce usable 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 nanofiltration pilot plant was installed at the factory; this provided valuable results regarding experimental nanofiltration membranes.

For the purpose of this study, UF membranes were used to "wash" the wine lees slurry at different solids concentrations. The KHT-rich permeate collected from UF was then concentrated using RO and nanofiltration to allow subsequent precipitation of the product (Fig. 1.2).

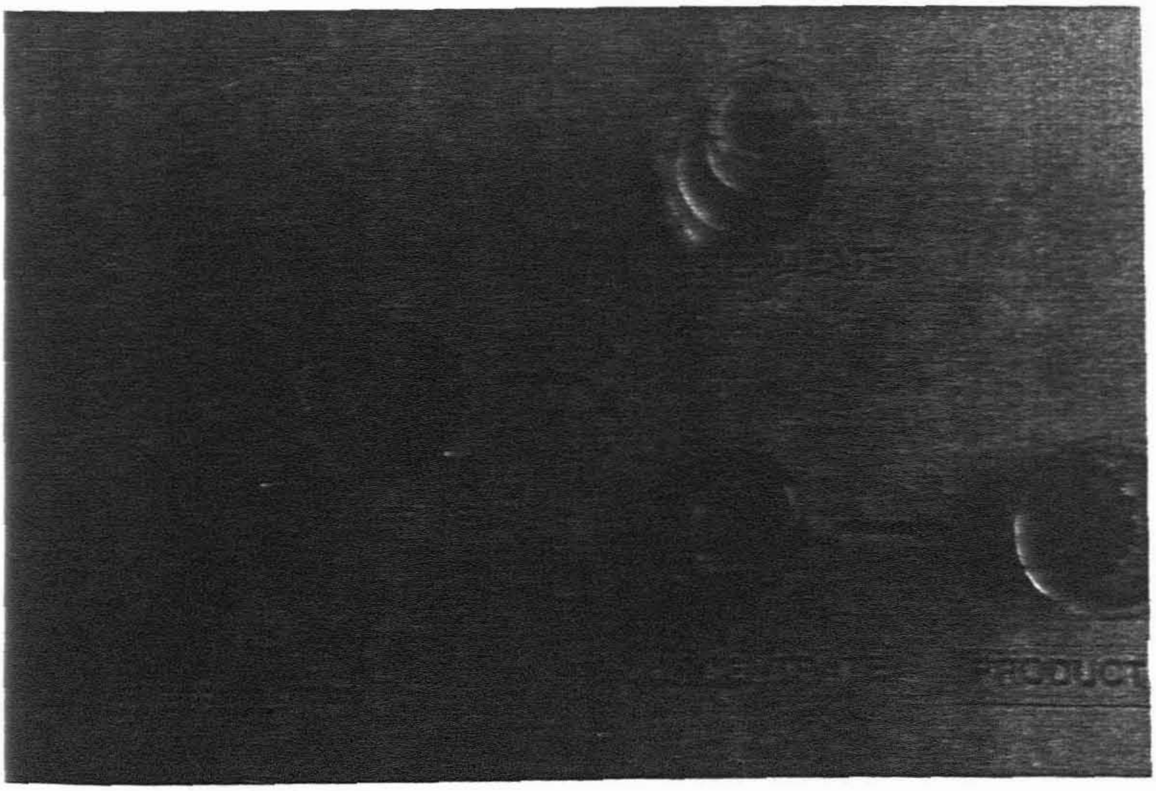


Fig. 1.2:

Potassium bitartrate extraction using UF and RO.

1.3.4 GEL POLARIZATION

From the results obtained when testing the membranes on industrial effluents, it became clear that a flux decrease was evident after a certain period of time. In the case of UF membranes, a decrease in flux was coupled with an unexpected salt retention. Although this could be the result of a number of factors, gel polarization could be the cause of the above mentioned deviations. Gel polarization is the complication that arises when hydrocolloids (such as proteins) and other large solutes or particles are ultrafiltered. These compounds, being largely retained by the membrane, tend to form fairly viscous and gelatinous layers on the membrane surface, so that a further resistance to flow of permeate is created. A study on different MMCO membranes was done to determine to what extent this phenomenon affected the membrane performance.

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 with 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. 2.2].

Although water treatment processes are usually used to produce potable water, they may be used to treat industrial feed-water and industrial effluents as well. As water consumption for domestic and industrial purposes increases, the quantity of treated effluent entering the environment increases. This means that an even larger percentage of our raw water supplies consists 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, i.e., 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 freely.

As mentioned in the definition of a membrane, the separation is achieved under the action of an external driving force. In the case of membranes that operate according to "sieving" mechanisms, such as microfiltration and ultrafiltration, 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 its size in relation to that of the pores in the membrane. However, the UF and MF membranes do not retain salt. In the case of nanofiltration and reverse osmosis 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 membrane systems are concentration gradient as in the case of dialysis, and electrical potential gradient as utilized in the case of electrodialysis.)

Membranes are available in two basic configurations, namely, tubular and flat-sheet. These membranes 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 (Fig. 2.2) 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 with sponge balls.

The capillary (Fig. 2.3 and 2.4) and hollow-fine fibre tubular membranes and the flat-sheet configurations (i.e. spiral-wound configurations) are attractive for their high membrane area-to-volume packing densities, but are not often used for wastewater treatment. 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 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 fluxes when membrane fouling has occurred.

Figure 2.5 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, i.e., reverse osmosis, ultrafitration, microfiltration, dialysis, and electrodialysis, cover a wide size-range, matched in versatility only by centrifugal processes [Ref. 1.1]. However, an absolute requirement for centrifugal processes is a suitable difference between densities of the two phases that are to be separated, in addition to the need for the two phases to be immiscible. Membrane separation processes have no such requirements. The real worth of membrane processes is that they permit separation of dissolved species of size down to the ionic range, provided the appropriate membrane operation is used.

What distinguishes the more common membrane operations, i.e., microfiltration, ultrafiltration, and reverse osmosis, is the application of hydraulic pressure to effect solvent and solute transport through the membrane (Fig. 2.6). However, the nature of the membrane itself controls which component permeates and which component is retained. Ideally, in reverse osmosis all components other than the solvent itself are retained, whereas in ultrafiltration only macromolecules or particles larger than approximately 0,001 μm to 0,02 μm are retained [Ref. 1.1]. Microfiltration processes, on the other hand, are designed to retain particles in the "micron" range, that is, suspended particles in the range of 0,1 μm to about 10 μm.

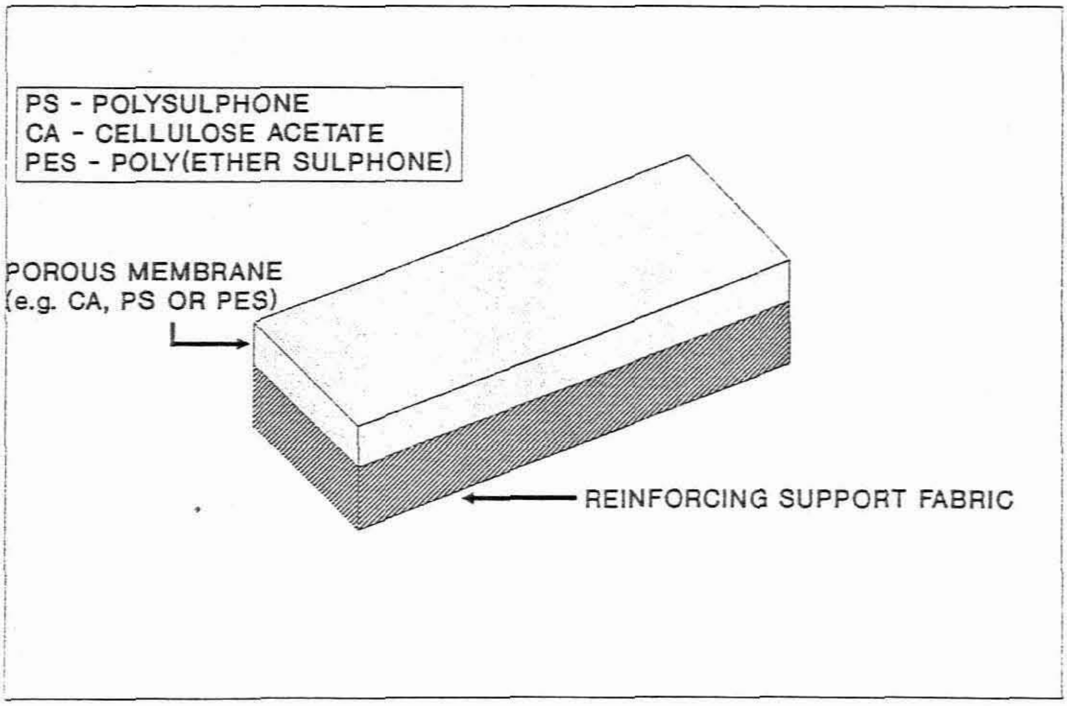


Fig. 2.1:
Cross-section of a tubular or flat-sheet membrane.

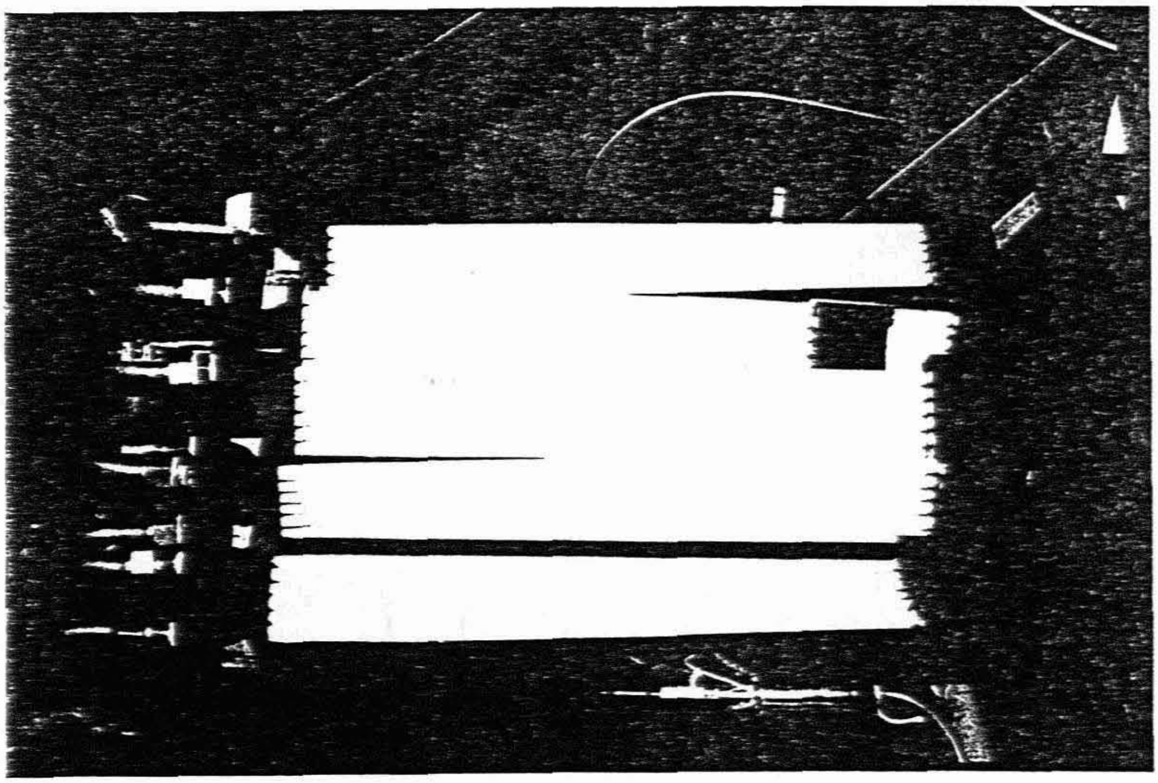
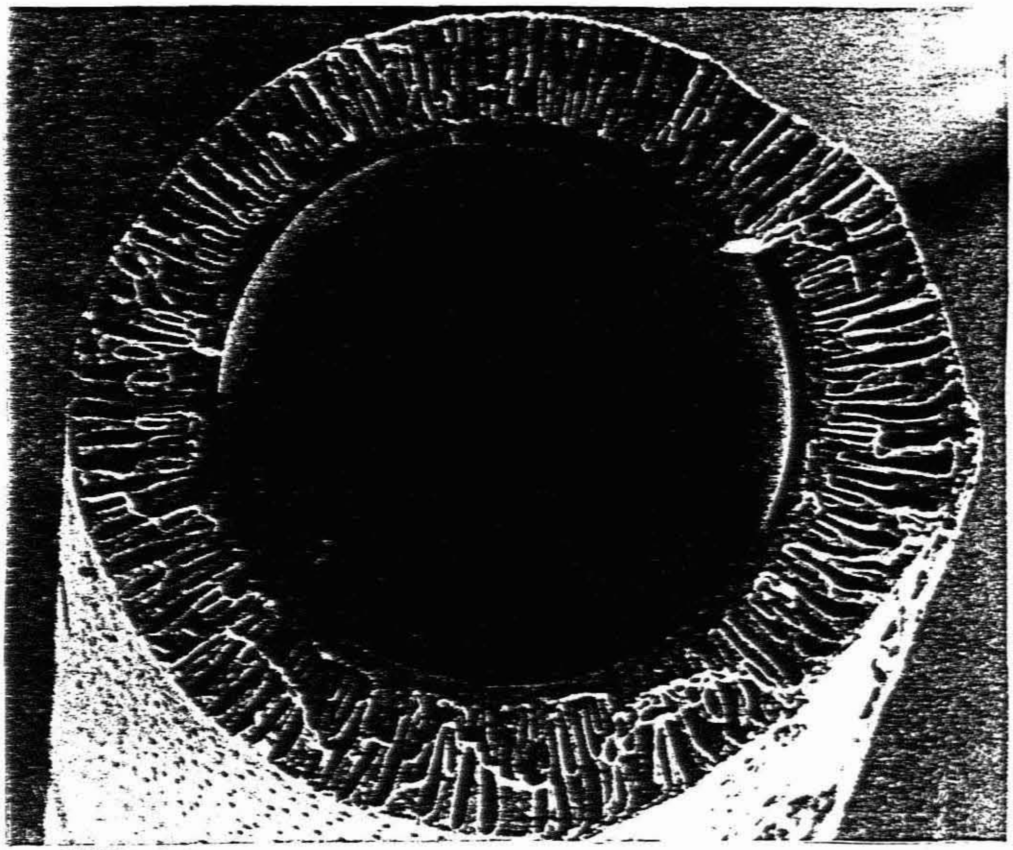


Fig. 2.2:
Tubular membranes.



Courtesy of WRC project

Fig. 2.3:
A SEM photograph of the cross-section of a capillary UF membrane.

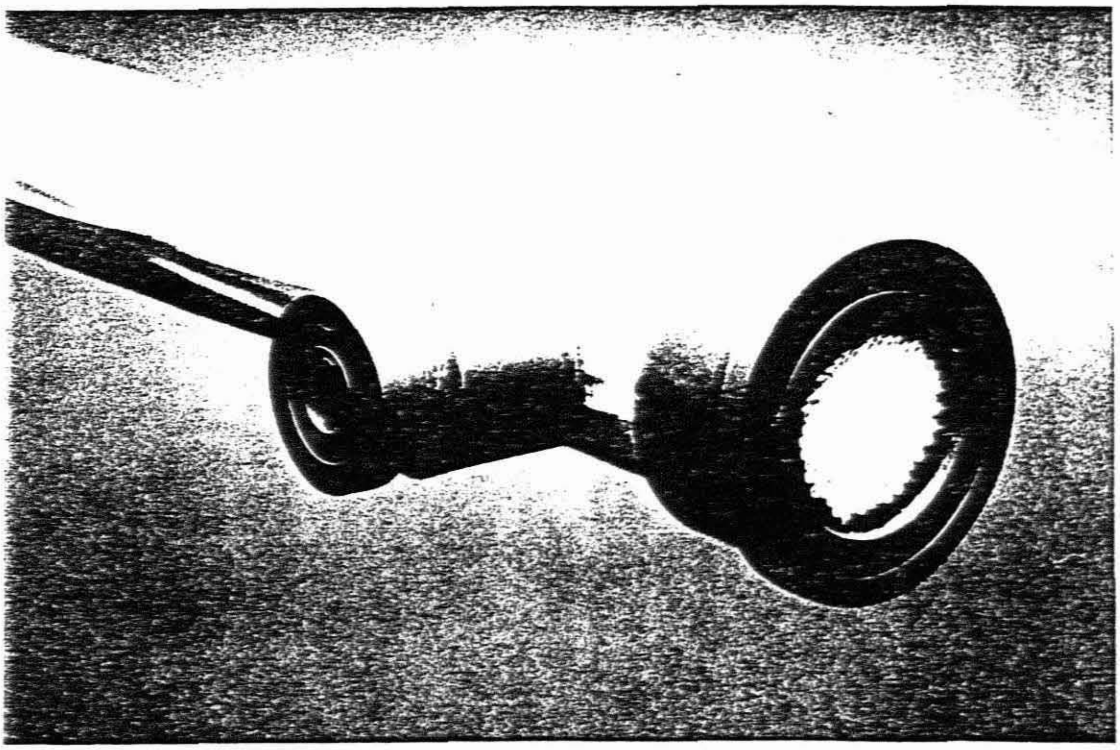


Fig. 2.4:
Capillary-membrane module prototype.

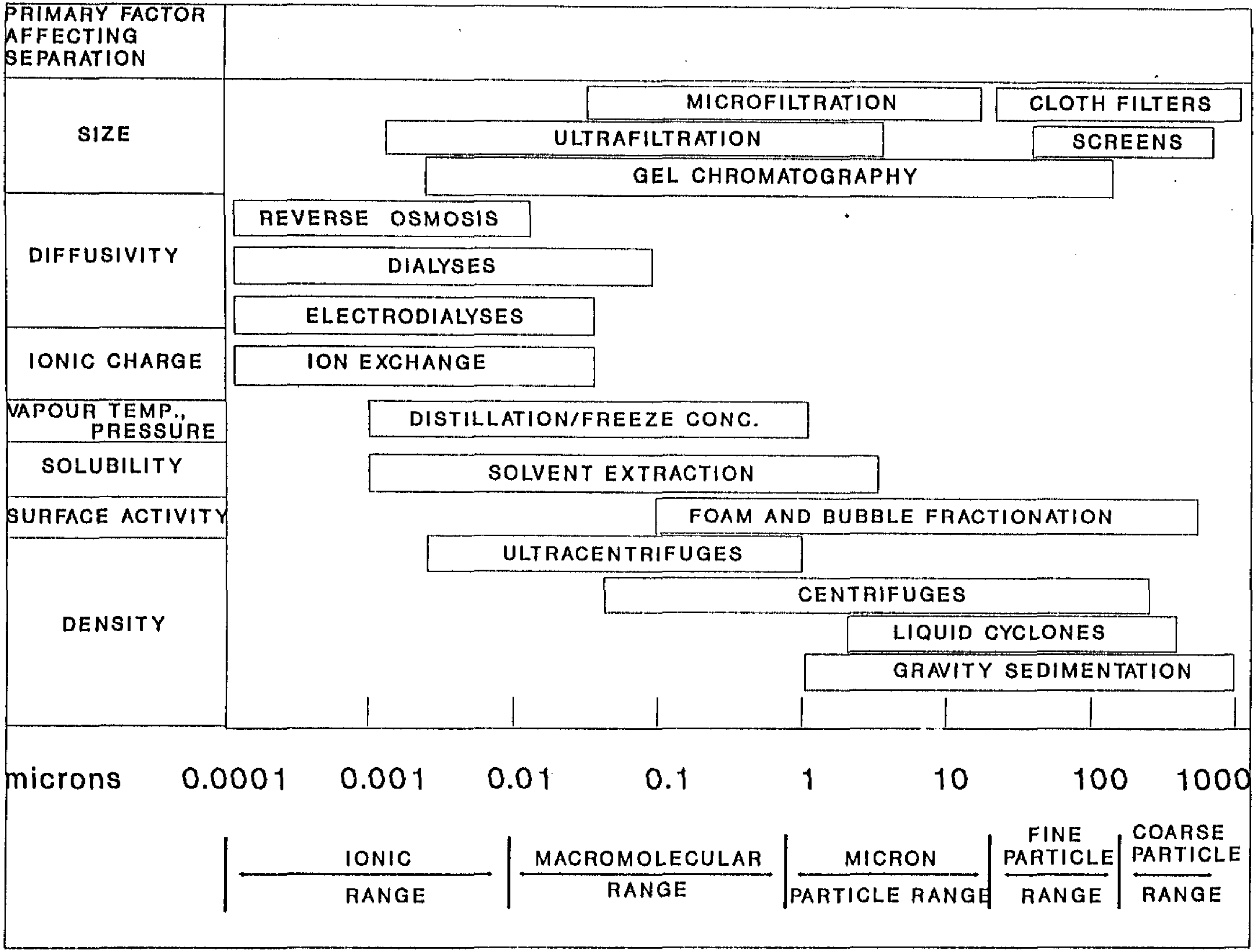


Fig. 2.5: Useful range of separation processes, showing the range of particle or molecular sizes covered by each process, and the primary factor governing each separation process.

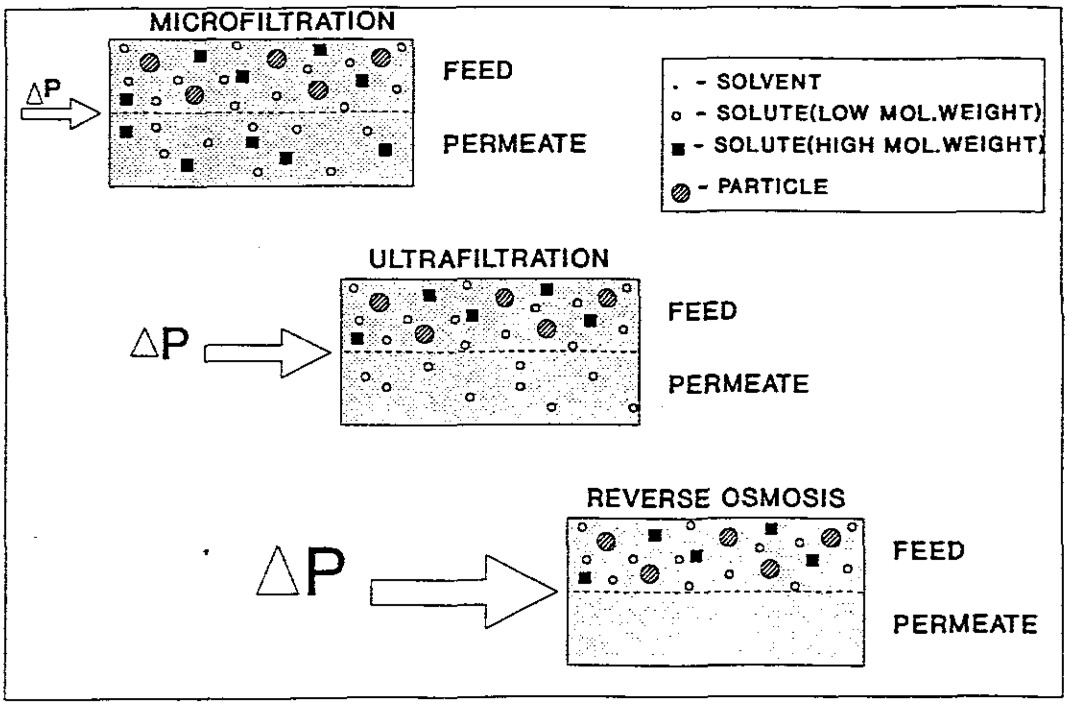


Fig. 2.6:
Schematic representation of microfiltration, ultrafiltration and reverse osmosis separation operations.

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, reverse osmosis is essentially a dewatering technique, while ultrafiltration can be regarded as a method for simultaneously purifying, concentrating and fractionating macromolecules or fine colloidal suspensions.

2.3 MICROFILTRATION

2.3.1 BACKGROUND

In filtration, two modes of operation exist, that is, dead-end filtration and cross-flow filtration (Fig. 2.7). In dead-end filtration the feed flow is perpendicular to the membrane surface, so that the retained particles accumulate and form a cake layer at the membrane surface. The thickness of the cake layer increases with filtration time and consequently the permeation rate decreases with increasing cake layer thickness. The pressure drop across the layer similarly increases with time. In cross-flow filtration this does not happen to the same extent, as the scouring action of the fluid in cross-flow motion has a limiting effect on the thickness to which the gel-layer can build up. Initially, the flux will decrease rapidly, but a steady-state gel-layer thickness is soon attained. The pressure drop follows the same trend if secondary resistance due to adsorption does not prove to be predominant. The thickness of this initial layer is a function of the membrane permeability, cross-flow velocity and process fluid [Ref. 2.3].

Microfiltration is the membrane process which most closely resembles conventional coarse filtration (e.g., sand filtration). The pore sizes of microfiltration membranes range from 10 to 0,05 μm, making the process suitable for retaining suspensions and emulsions. Microfiltration membranes may be prepared from a large number of different materials based on either organic materials (polymers) or inorganic materials (ceramics, metals, glasses) (Fig. 2.8).

The main problem encountered when microfiltration is applied is flux decline caused by concentration polarization, gel polarization and fouling. The latter is caused by the deposition of solutes inside the membrane pores or on the membrane surface. Considerable flux decline can be observed in most cases when these membranes are applied to treatment of a process stream.

Adsorption phenomena play an important role in fouling and hence it is important to select an appropriate membrane material. Membranes made from hydrophobic materials such as polysulphone and polyethersulphone have in general a greater tendency to foul, especially in the case of an effluent containing hydrophobic substances such as proteins or oils.

2.3.2 APPLICATIONS

Microfiltration is applicable in various separation, concentration and fractionation processes. Microfiltration has been successfully introduced in a number of industrial applications and has gained commercial acceptance.

Applications for microfiltration include:

(i) industrial wastewater treatment [Ref. 1.2 and 2.4] - these applications include mostly effluents containing high concentrations of suspended solids [Ref. 2.5],

(ii) treatment of domestic waters e.g. total organic carbon removal (as soap) in domestic water by microfiltration [Ref. 2.6],

(iii) sewage effluent treatment [Ref. 2.7],

(iv) treatment of effluents from food and beverage industry, for example:
- dairy applications - MF has roles in the removal of fat from whey prior to UF or other processes [Ref. 2.8],
- gelatin concentration - microfiltration is utilized to remove dirt from gelatin solutions prior to concentration (which is done by UF or evaporation) [Ref. 2.9],
- filtration of syrups and sweeteners [Ref. 2.9],

(v) microfiltration in the semiconducter industry - for the removal of particulate contaminants in process fluids [Ref. 2.10].

Table 2.1 illustrates various other applications for microfiltration [Ref. 2.11].

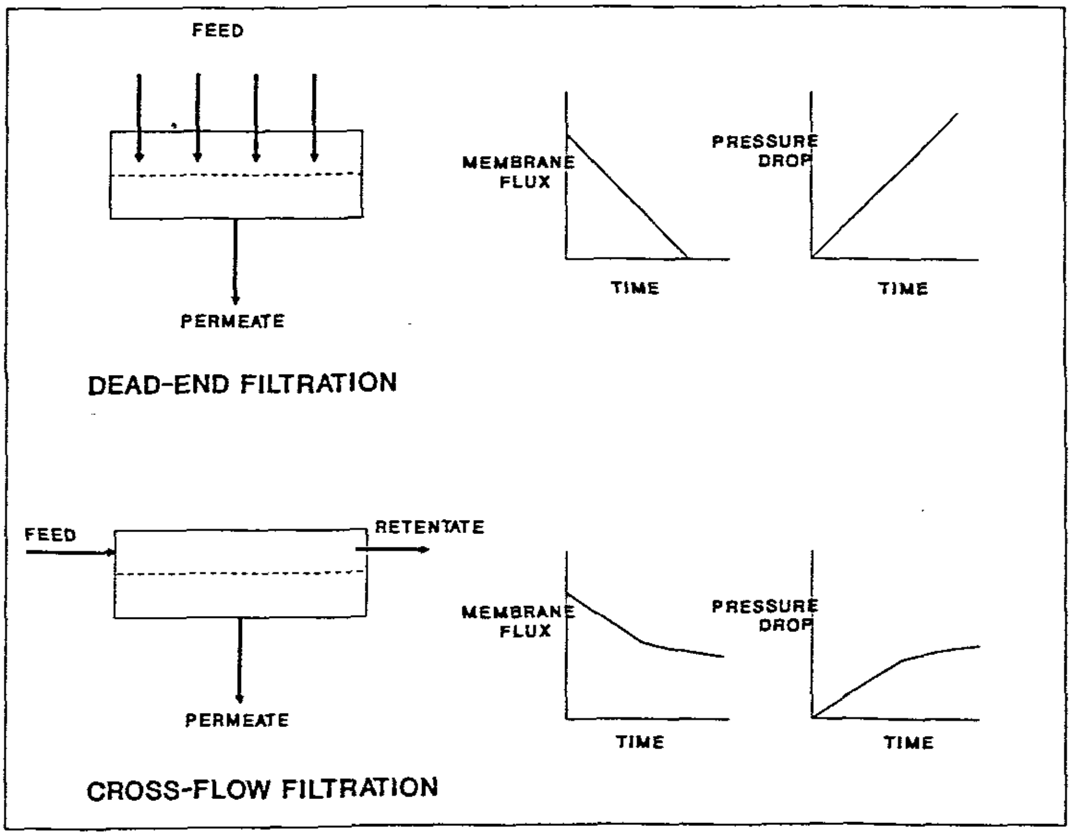


Fig. 2.7:
Dead-end and cross-flow filtration.

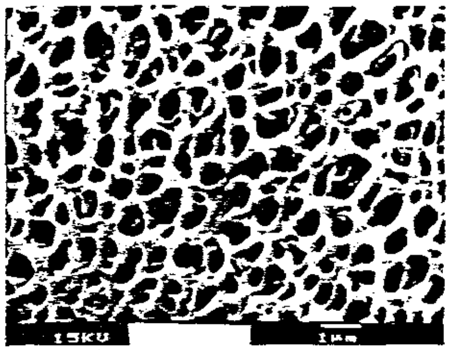


Fig. 2.8:
SEM photograph of a polymeric microfiltration membrane.

TABLE 2.1: CURRENT MICROFILTRATION PROCESS APPLICATIONS

Application	Customers	Equipment Type	Competing Processes	Problems
Haze removal from gelatin	Food companies	Spiral-wound, plate-and-frame	Diatomaceous earth filtration	High viscosity, very high protein passage required
Dextrose clarification	Corn refiners	Spiral-wound, plate-and-frame	Diatomaceous	High viscosity permeate
Wine	Wineries	Spiral-wound, capillary, plate-and-frame	Asbestos	Fouling, yield, flavour
Beer bottoms recovery	Breweries	Spiral-wound, capillary, plate-and-frame	Centrifuge	Foam stability, flavour
Bright beer sterilization	Breweries		Pasteurization	Reliability, Huge market potential
Pharmaceutical/ Biological	Biotech and Pharmaceutical companies	Dead-end filtration		Market huge, but usually done on a smaller scale than others

2.4 ULTRAFILTRATION

2.4.1 BACKGROUND

Ultrafiltration is a membrane process whose separation performance lies between that of reverse osmosis and microfiltration. The size of the pores in the membranes ranges from 0,1 μm to 0,005 μm. Ultrafiltration is typically used to retain macromolecules from a solution, the lower limit being solutes of molecular mass of a few thousand Daltons. Ultrafiltration and microfiltration membranes can both be considered as porous membranes where retention is determined mainly by the size and shape of the solutes relative to the size of the pores in the membrane. Furthermore, transport of the solvent through the membrane is directly proportional to the applied pressure [Ref. 2.3].

Cross-flow operation is, as in the case of microfiltration, applicable to ultrafiltration. Because of this, it is less susceptible to membrane fouling than conventional dead-end filtration.

Most ultrafiltration membranes used commercially are prepared from polymeric materials by a phase-inversion process. Polysulphone, polyethersulphone and sulphonated polysulphone are some of the materials used regularly in the manufacture of these membranes [Ref. 2.3] (see Fig. 2.9 and 2.10).

Ultrafiltration is often used for the fractionation of macromolecules where large molecules have to be retained by the membrane, while small molecules permeate freely. In order to choose a suitable membrane, manufacturers often use the concept of molecular mass "cut-off" (MMCO). However, it should be realised that molecular mass of a retained species is not the only criterion that determines selectivity. As in the case of microfiltration, the effect of concentration polarization is real. This phenomenon is mainly influenced by the type of process stream operated on, the linear flow velocity of the feedstream, operating conditions and membrane configuration.

Many factors affect the rate of permeate flow through a membrane; operating temperature and pressure are two of them. An increase in temperature reduces the viscosity of the feed liquid and thereby increases the flux. The operating pressure ranges from 200 to 600 kPa for most ultrafiltration applications and membrane flux is conditionally proportional to the operating pressure.

As in the case of microfiltration the process performance is not directly related to the intrinsic membrane properties. The reason for this is the occurrence of concentration polarization and fouling. Because the membrane is porous, there is a continuous convective flow of solvent (i.e. water) towards the membrane surface. The macromolecular solute retained by the membrane accumulates at the surface of the membrane while the water passes through it, resulting in a concentration build-up on the membrane surface. The solute can return to the bulk of the stream only by diffusion. An imbalance between two opposing forces is created, namely, convective transport towards the membrane and diffusive transport away from the membrane. At steady-state, the convective flow of the solute to the membrane is equal to the diffusional backflow from the membrane to the bulk.

When operated under polarized conditions, a further increase in pressure will not result in an increase in flux because the resistance of the gel-layer increases so that a limiting flux value J_L is attained [Ref. 2.3] (see Fig. 2.11).

2.4.2 APPLICATIONS

Ultrafiltration is used in numerous applications which involve situations where high molecular mass components have to be separated from low molecular mass components. Applications can be found in fields such as the food, dairy, pharmaceutical, textile, chemical, metallurgy, paper, and leather industries [Ref. 2.12]. Table 2.2 shows the principle applications of ultrafiltration [Ref. 2.13].

Applications for ultrafiltration include:

(i) UF as pretreatment method to RO desalination [Ref. 2.14],

(ii) sewage effluent treatment [Ref. 2.15] - a combination of ultrafiltration with biological treatment by activated sludge has been pioneered commercially by Dorr Oliver Inc. [Ref. 2.16],

(iii) treatment of lake water for potable water production e.g. the use of UF for removal of turbidity, dissolved organic carbon and ultraviolet absorbing materials from water [Ref. 2.17],

(iv) treatment of industrial wastewater [Ref. 1.2, 2.4 and 2.18] in, for example:
- the paper manufacturing industry [Ref. 2.19],
- the fishing industry [Ref. 2.20],
- olive mills waste water treatment [Ref. 2.21],

(v) production of boiler-feed quality water from oil-in-water emulsions [Ref. 2.22],

(vi) treatment of textile industry effluents in conjunction with RO [Ref. 2.23 and 2.24],

(vii) the utilizing of UF in the food, dairy and beverage industry [Ref. 2.25], for example:
- isolation and concentration of vegetable proteins [Ref. 2.26] and decolourization of Hydrolysis Vegetable Protein [Ref. 2.27],
- the separation of milk proteins (caseins) and fat from lactose and salts in the dairy industry [Ref. 2.28, 2.29 and 2.30],
- concentration of skimmed milk by ultrafiltration [Ref. 2.31 and 2.32],
- fruit juice clarification by ultrafiltration [Ref. 2.33 and 2.34],
- grape must and wine processing by ultrafiltration [Ref. 2.35 and 2.36],
- the removal of starch, waxes, colour compounds and suspended solids in cane juice (in sugar refineries) [Ref. 2.37],
- protein recovery from wheat starch by UF [Ref. 2.38],

(viii) medical applications, e.g. artificial kidney dialysis [Ref. 2.39],

(ix) separation by ultrafiltration of peptides and proteins in the drug industry [Ref. 2.40].

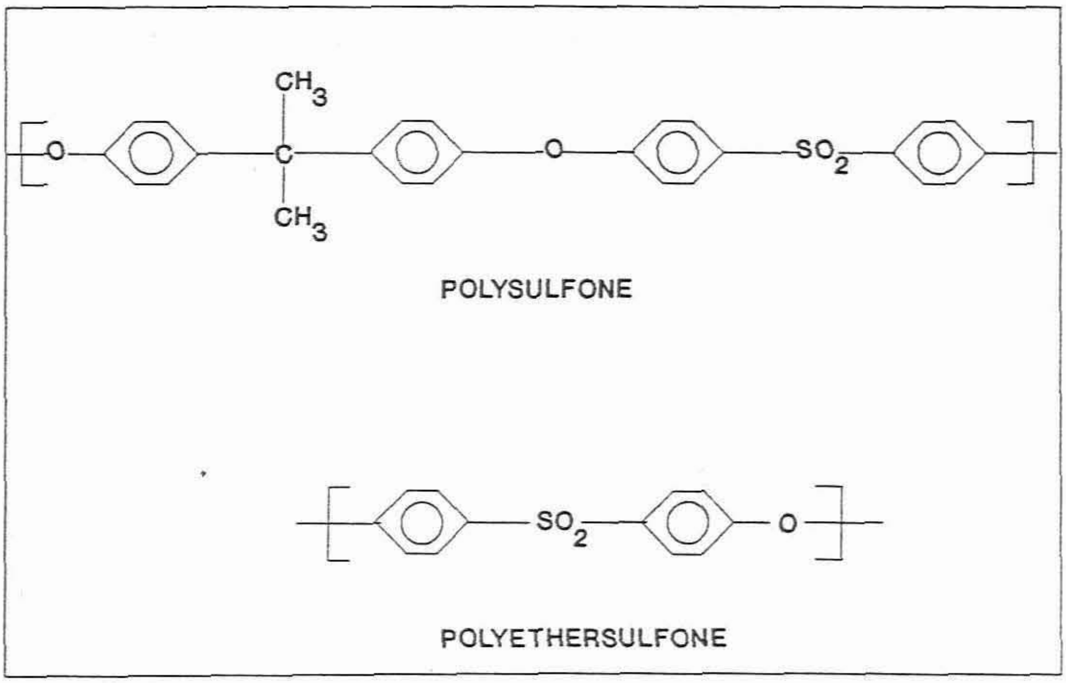


Fig. 2.9:
Chemical structure of PS and PES.

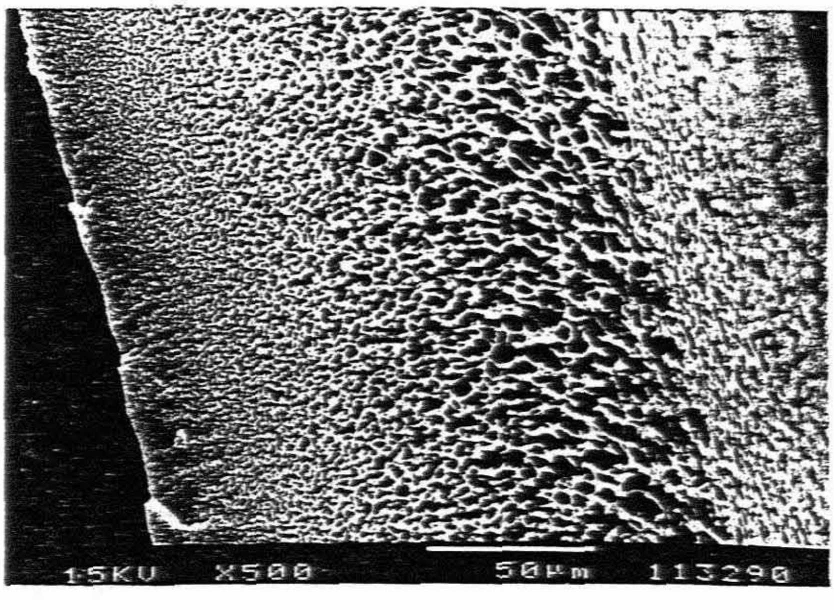


Fig. 2.10:
A SEM photograph showing the cross-section of an ultrafiltration polysulphone membrane (magnified 1000 times).

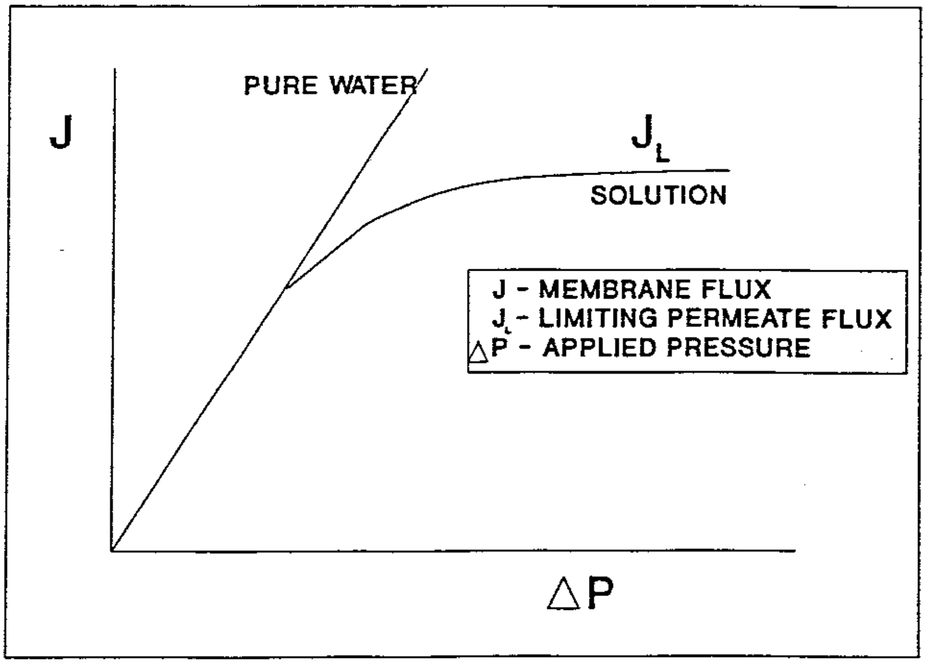


Fig 2.11:
Relationship between flux and applied pressure in ultrafiltration.

TABLE 2.2: PRINCIPAL APPLICATIONS OF ULTRAFILTRATION

Application	Customers	Leading Membrane	Leading Supplier
Ultrafiltration of electropaint wastewater for paint recovery	auto, appliance firms, etc.	tubular spiral plate-&-frame capillary	Koch Rhone-Poulenc Asahi Romicon
Recovery of protein from cheese whey	dairies	spiral plate & frame	Koch DDS
Ultrafiltration of milk to increase cheese yield	dairies	spiral plate & frame	Koch DDS
Concentration of oils and emulsions for pollution abatement	metal cutting and forming, can makers industrial laundries	tubular plate-&-frame capillary	Koch Rhone-Poulenc Romicon
High-purity water	chip producers	capillary spiral	Asahi Nitto Osmonics
Pyrogen removal	pharmaceutical glucose producers	capillary	Asahi Romicon
Size recovery	textile firms	spiral	Koch
Enzyme recovery	enzyme producer biotech	plate-&-frame capillary	DDS, Koch Romicon
Gelatin concentration	food firms	spiral	Koch
Juice clarification	fruit processors	tubes,capillary capillary ceramics	Koch, Romicon Alcoa
Pharmaceutical	drug firms	plate & frame spirals	DDS Koch
Latex	chemical firms (PVC, SBR)	tubes	Koch Kalle

2.5 NANOFILTRATION

2.5.1 BACKGROUND

Nanofiltration (NF) is a pressure-driven liquid-phase membrane process in which finely microporous membranes are used. NF membranes are thought to have pores in the range of 2 to 15 nm, which places them between ultrafiltration and reverse osmosis membranes. The characteristic of NF membranes that distinguishes them from RO and UF membranes is that they exhibit different retentions for different ionic species. The performance of NF membranes falls between the high salt permeability of UF membranes and the high salt retention of RO membranes, which allows the simultaneous concentration and desalting of organic solutes with a minimal loss of solute to the permeate. The NF membranes also show water fluxes that lie between those of RO and UF. This high flux for membranes that can retain divalent metal ions, makes NF attractive for specialized metal-separation processes, such as the treatment of plating wastes [Ref. 2.41].

2.5.2 APPLICATIONS

Nanofiltration membranes have many potential industrial applications. These include the treatment of aqueous streams from the chemicals industries, the treatment of acidic and basic streams, treatment of pulp and paper streams, the treatment of pharmaceutical processing streams and the treatment of spent paint sludges [Ref. 2.42].

In the plating industry the rinse water poses a problem because it contains concentrations of metal ions that are too low to recycle back to the plating bath and are too high to be disposed due to possible damage to the environment. NF provides a possible solution by allowing the valuable metal ions to be concentrated for recycling, while at the same time producing water for re-use or discharge into the environment [Ref. 2.41].

Nanofiltration is also reported to be used as an alternative process to traditional clarification in water treatment in cases where removal of micropollutants and micro-organisms is required [Ref. 2.43].

Commercially available nanofiltration membranes have also been used to treat cotton dyehouse effluents [Ref. 2.44].

2.6 REVERSE OSMOSIS

2.6.1 BACKGROUND

Reverse osmosis is a unique form of filtration with the ability to separate dissolved solids from a solution. RO is used when molecular solutes such as inorganic salts have to be separated from a solution.

Osmosis is the operation by which a semi-permeable membrane allows the passage through it of the solvent (usually water), while it restricts the passage of solute particles. An osmotic pressure arises when two solutions of different concentrations are separated by a membrane which is permeable to the solvent but impermeable to the solute. As illustrated in Figure 2.12 and Figure 2.13, the solvent from the less concentrated solution travels through the membrane and will continue doing so until it equals the head of the apparent osmotic pressure of the concentrated solution. In the case of reverse osmosis, the opposite happens; an external pressure larger than the osmotic pressure of the concentrated solution is exerted upon the solution. The solvent (water) will flow in the direction of the less concentrated solution in an attempt to establish the reverse osmotic equilibrium. The concentrated solution will thus become more concentrated as solvent passes through the membrane.

Solutions containing low-molecular mass solutes have a much higher osmotic pressure than macromolecular solutions used in UF. In order that water will pass through the membrane, the applied pressure has to be higher than the osmotic presssure of the solution (Fig. 2.13) [Ref. 2.3]. The pressures used in RO range from 2 MPa to 10 MPa.

Figure 2.14 shows typically the effect of pressure, temperature, and water recovery on the membrane flux and product quality of RO membranes. These results are however generalized and deviations can be expected when different industrial streams or effluent concentrations are used as feed [Ref. 2.45].

Two types of RO membrane were used in this study. An established cellulose acetate (CA) membrane was used in most experiments as control against the experimental nanofiltration (NF) and ultra-thin-film RO (UTF RO) membranes. The UTF RO membranes were manufactured by an interfacial condensation reaction which results in a very thin crosslinked film on a substrate membrane. The manufacture of these membranes is discussed in more detail in Chapter 3.

2.6.2 APPLICATIONS

There is a wide range of applications for reverse osmosis. In most cases reverse osmosis is used for solvent (water) purification and solute concentration. In the case of solvent purification, the permeate would be the product, whereas in solute concentration the concentrated feed would be the product. Most of the applications are in the purification of water, for example, in the desalination of brackish water or seawater to produce potable water [Ref. 2.46]. Brackish water has been desalinated by RO on a commercial scale since the early 1970s [Ref. 2.47]. Desalination of seawater by RO is more difficult than of brackish water [Ref. 2.48] as retentions must be approximately 98% in order to obtain a suitable product. The amount of salt present in brackish water is between 1 000 and 5 000 ppm, while the salt concentration in seawater is in the region of 35 000 ppm. It can therefore be seen that in the case of seawater desalination, high operating pressures would be needed to overcome the osmotic pressure of the seawater, and therefore operating costs will be higher than for brackwater desalination. The comparative economics of seawater and brackish water desalination have been discussed by Glueckstern and Kantor [Ref. 2.49]. Desalination of seawater by RO is estimated to be two to three times more costly than desalination of brackish water. However, the RO process is still considered to be one of the least expensive methods for desalinating seawater.

Although the original purpose behind the development of RO membranes was the desalination of seawater, desalination of brackish water and purification of industrial water have emerged as the main applications of RO [Ref. 2.47 and 2.50]. Although RO is mainly used as a means to purify water, it is also utilized as a separation technique for a wide variety of purposes [Ref. 2.51 and 2.52].

Applications for RO include:

(i) dichromate recovery chrome-plating rinse baths [Ref. 2.53],

(ii) the treatment of industrial wastewaters [Ref. 2.54],

(iii) treatment of polluted rivers [Ref. 2.55, 2.56, 2.57, 2.58 and 2.59),

(iv) applications in the food and beverage industry [Ref. 2.60], for example:
- the fractionation of cheese whey [Ref. 2.61 and 2.62],
- concentration of sugar solutions e.g. cane suger, beet juice, maple syrup and corn syrup [Ref. 2.61],
- concentration of fruit juices e.g. orange, apple, tomato, etc. [Ref. 2.63, 2.64 and 2.65],

(vi) desalination of seawater and brackish waters e.g. seawater desalination plant in Jeddah, Saudi Arabia [Ref. 2.66 and 2.67],

(vii) sewage effluent treatment - a plant is currently used in Port Elizabeth (RSA) for the reclamation of secondary sewage effluent [Ref. 2.68],

(viii) treatment of domestic and municipal waters [Ref. 2.55 and 2.57],

(ix) treatment of paper and pulp effluents [Ref. 2.69, 2.70 and 2.71],

(x) electroplating industry - recovery of nickel, brass cyanide, chromic acid and chromium is currently being done by RO [Ref. 2.72],

(xi) treatment of textile industry effluents with RO in conjunction with UF [Ref. 2.23 and 2.24],

(xii) other applications mentioned by Slater et al. [Ref. 2.54] and Delyannis [Ref. 2.55] include: treatment of wastewater from electro-painting, treatment of petrochemical complex wastewaters and treatment of wastewater from the pharmaceutical industry.

Table 2.3 shows more applications for RO [Ref. 2.45].

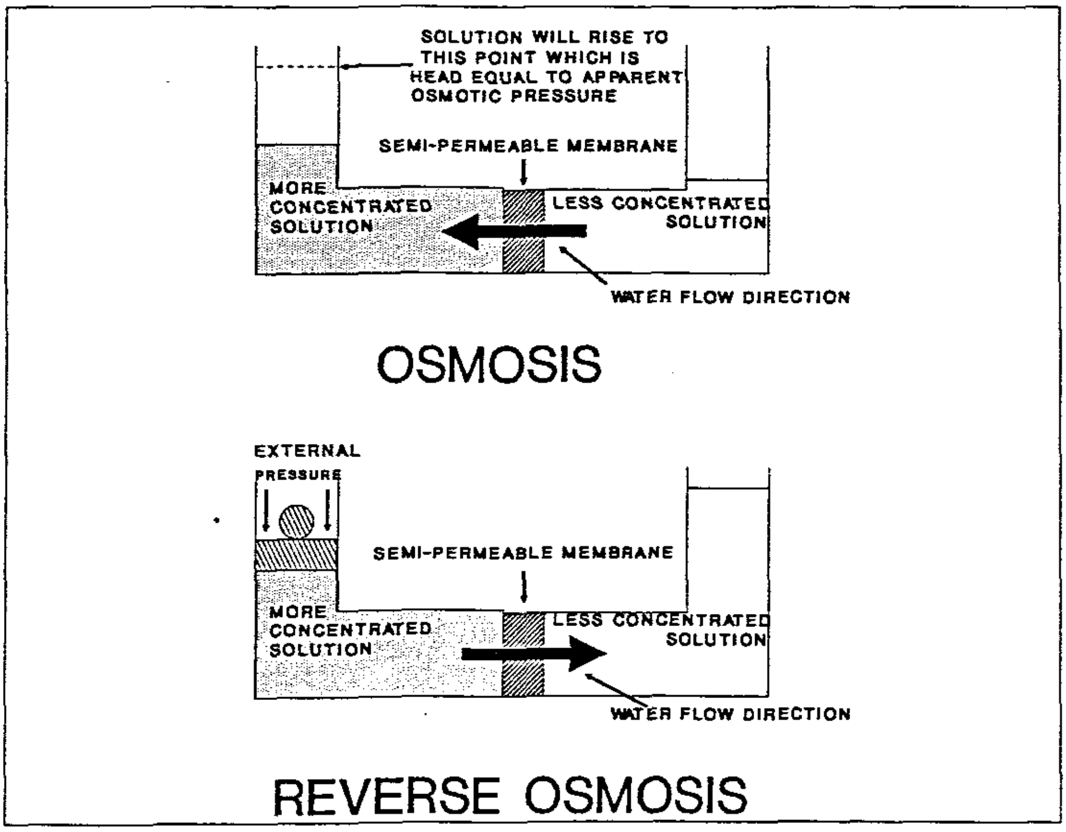


Fig. 2.12:
Osmosis/Reverse Osmosis.

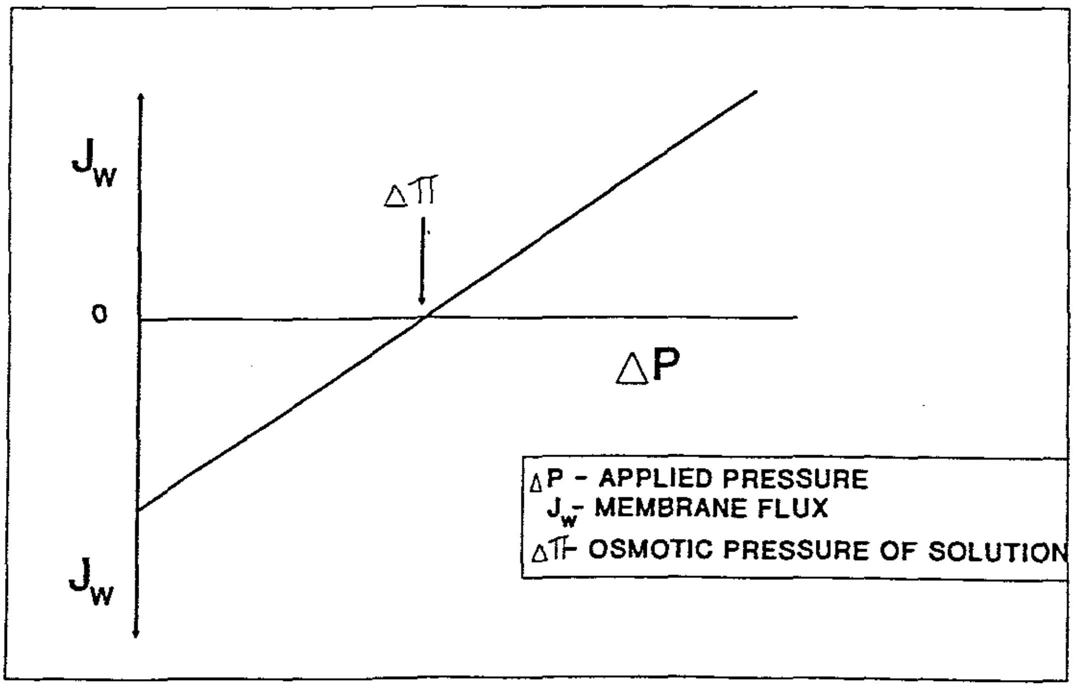


Fig. 2.13:
Plot of water flow (J_W) as a function of applied pressure.

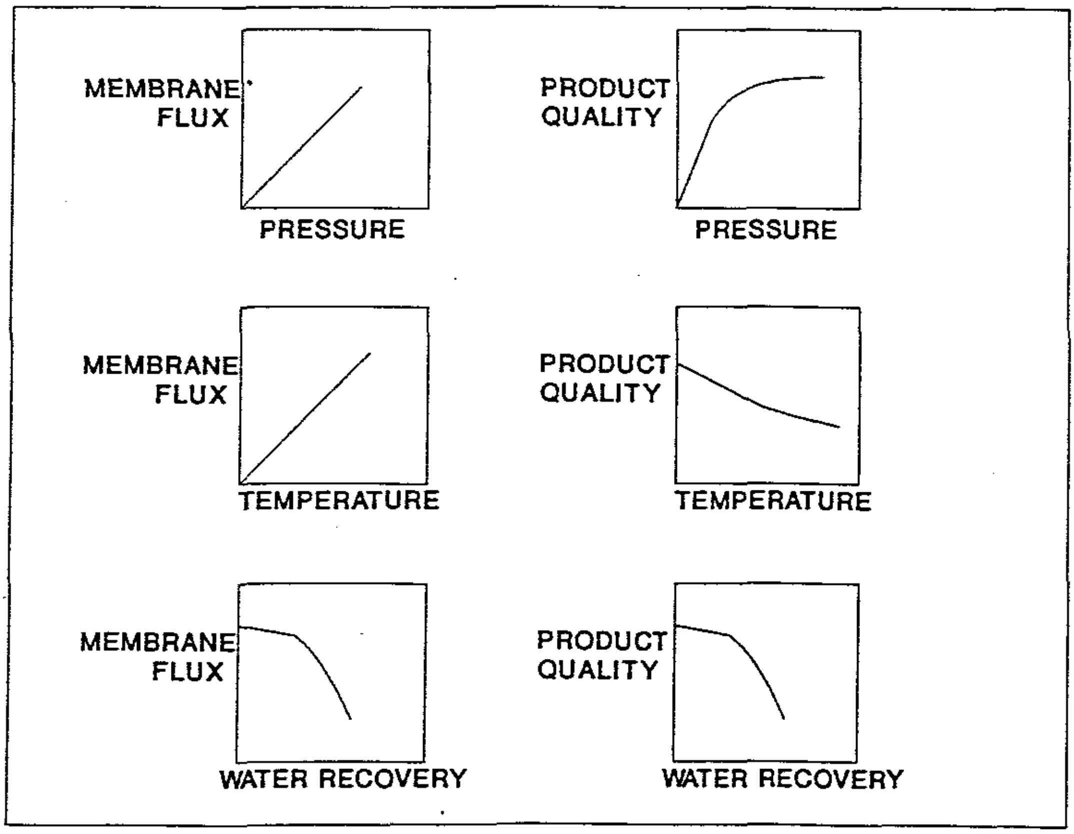


Fig. 2.14:

Effects of applied pressure, feed temperature, and water recovery on the membrane flux and product water quality for RO membranes.

TABLE 2.3 : REVERSE OSMOSIS MARKET APPLICATIONS

Status	Industry	Applications
Mature	Desalination	Potable Water Production Seawater Brackish Water Municipal Wastewater Reclamation
	Ultrapure Water	Semiconductor Manufacture Pharmaceuticals Medical Uses
Growing	Utilities and Power Generation	Boiler Feedwater Cooling Tower Blowdown Recycle
	Point of Use	Home Reverse Osmosis
Emerging	Chemical Process Industries	Process Water Prod. and Reuse Effluent Disposal Water Reuse Water/Organic Separation Organic Liquid Mixtures sepn.
	Metals and Metal Finishing	Mining Effluent Treatment Plating Rinse Water Reuse Recovery of Metals
	Food Processing	Dairy Processing Sweeteners Concentration Juice and Beverage Processing Light Beer and Wine Prod. Waste Stream Processing
	Textiles	Dyeing and Finishing Chemical Recovery Water Reuse
	Pulp and Paper	Effluent Disposal Water Reuse
	Biotechnology/ Medical	Fermentation Products Recovery Purification
	Analytical	Isolation, Concentration, and Identification of Solutes and Particles
	Hazardous Substance Removal	Removal of Environmental Pollutants from Surface and Groundwaters

2.7 CALCULATIONS

The following calculations were done regularly during this study.

2.7.1 MEMBRANE FLUX

Membrane flux refers to the volume of solvent transport through the membrane per unit time.

2.7.1.1 *TUBULAR MEMBRANES*

Flux is measured in $\ell/m^2.h$ (LMH).

$$\text{Membrane flux (LMH)} = \frac{V}{(A \times t)} = \frac{V}{L(\pi \times d) \times t}$$

Where: V = volume (ℓ)

A = membrane area (m^2)

t = time (hours)

L = tubular membrane length (m)

d = inside diameter of the tubular membrane (m)

2.7.1.2 *MODULES (TUBULAR OR CAPILLARY)*

$$\text{Membrane flux (LMH)} = \frac{V}{(A \times t)} = \frac{V}{L(\pi \times d) \times N \times t}$$

Where: N = Total number of membrane tubes in the module.

(In this study capillary membranes were tested in the parallel module configuration only.)

2.7.2 RETENTION

Retention refers to the percentage solute retained by the membrane.

$$\text{Retention} = \frac{(Cf - Cp)}{Cf} \times 100$$

Where: Cf = feed concentration [kg/m^3]

Cp = permeate concentration [kg/m^3]

In the case of RO membranes the conductivity was measured and used to calculate conductivity retention.

To determine the retention of organic solutes or macromolecules (as in the case of ultrafiltration), measured feed and permeate samples were evaporated to complete dryness and weighed in order to determine the organic content of the permeate and feed. Organic retention could then be calculated using a formula analogous to the above.

2.7.3 LINEAR VELOCITY

Linear velocity of the feedstream across the membranes plays an important role, especially when the role of gel-layer formation, the existence of a boundary layer, and fouling are considered. It was therefore important to keep the linear velocity constant during the tests. A specific velocity was selected for each specific membrane operation and the volumetric flowrate was calculated in litres per hour in order to set the test-rig to a fixed flowrate.

$$Q = vAN = v \times \pi \times (d/2)^2$$

Where:

Q = volumetric flowrate (ℓ/h)
v = linear velocity (m/s)
A = cross-sectional area (m^2)
d = inside diameter of the tubular or capillary membrane
N = the amount of membranes per module (in the case of a capillary membrane module).

CHAPTER 3

FABRICATION OF TUBULAR UTF RO MEMBRANES FOR BRACKWATER TREATMENT

3.1. INTRODUCTION

Membratek, a company that specializes in the manufacture and installation of membranes, informed IPS of a possible opportunity for the on-site testing of RO membranes in Botswana. The objective of the operation was to desalinate brackish water to give a potable water which would comply with the SABS specification. The feedwater had the following characteristics:

(i) $CaSO_4$/NaCl-type water
(ii) TDS approximately 3000 mg/ℓ
(iii) High feedwater temperature - up to 38 °C
(iv) Free chlorine - nil.

The standards with which the membranes were to comply were that the membrane 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 conventional CA RO membranes while the Institute would provide them with experimental tubular ultra-thin-film RO membranes. These membranes had to be potted in 1,2 m modules by Membratek before installation at the site in Botswana.

Experimental UTF-RO CAMOH and CAMPIP membranes were previously manufactured and tested in flat-sheet and tubular configuration by M.J. Hurndall in a dissertation presented for her doctor's degree [Ref. 3.1].

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 to determine whether they complied with the desired standards,

(iv) select and scale up the production of the membranes which complied with the desired standards,

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

3.3. EXPERIMENTAL

3.3.1 PLANNING

A UTF-RO membrane consists of a thin and relatively brittle membrane layer on a substrate membrane. The membranes were made by using a 719 ultrafiltration membrane as substrate and dipping it in a PVOH solution. After dipping, the membranes were baked at elevated temperatures for a period of time, thus leaving a very thin crosslinked PVOH layer on the substrate membrane.

It was decided first of all to manufacture the membranes on a laboratory-scale thereby determining whether the membrane product met the desired standards, and to see whether it was possible to manufacture the UTF-RO CAMOH and CAMPIP membranes in tubular form. It was planned to fabricate and test the membranes in three different stages, namely:

(i) fabrication of membranes on small scale;
(ii) testing and evaluation of these membranes;
(iii) fabrication of membranes which met the desired standards, on a larger scale (to be sent to Membratek for module making).

3.3.2 MANUFACTURE OF MEMBRANES

3.3.2.1 *PVOH RO MEMBRANES - HOIPS*

A commercial 719 ultrafiltration membrane 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 (codes N in the table below). After draining it for a certain period of time, the membranes were again dipped into an isophthaloyl (IPC) or trimesoyl chloride (TMC) in hexane solution to effect crosslinking (codes X 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:

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

Where: N1 = 0,25 PVOH + 0,25 PIP + 0,5 NaOH (aqueous solution)

N2 = 0,5 PVOH + 0,5 PIP + 0,95 NaOH (aqueous solution)

N3 = 0,5 PVOH + 0,45 PIP + 0,05 TAB + 0,95 NaOH (aqueous solution)

N4 = 0,5 PVOH + 0,45 PIP + 0,05 CPA + 0,95 NaOH (aqueous solution)

M = N but with different manufacturing conditions.

And: X1 = 1% IPC in hexane

X2 = 1% TMC in hexane

X3 = 2% TMC in hexane

3.3.2.2 *PVOH-RO MEMBRANES - CAMOH AND CAMPIP*

In the fabrication of CAMOH and CAMPIP membranes the commercial 719 polysulphone substrate 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.

3.3.2.3 *PVOH-RO MEMBRANES - FURFURYL ALCOHOL/ISOPROPANOL*

A commercial 719 ultrafiltration membrane supplied by Membratek, were used as substrate. The membranes were dipped in the aqueous solution described below, drained and baked at temperatures of 130 to 150 °C.

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

codes F1LT and F1HT

Where F1 :	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

3.3.3 TEST RESULTS

3.3.3.1 *HOIPS MEMBRANES*

The membranes were tested on a 2 000 ppm NaCl feed solution at 30 bar, a linear velocity of 1,5 m/s and at 20 °C. As illustrated in Fig. 3.1, fluxes and retentions varied widely from one membrane type to another. The best results were obtained from membranes N1X1 and M1X1 with fluxes ranging from 20 to 30 LMH with corresponding NaCl retentions of 78 to 84%.

3.3.3.2 *CAMOH AND CAMPIP MEMBRANES*

As shown in Fig. 3.2 generally good results were obtained from the CAMOH and CAMPIP membranes with fluxes of 15 to 40 LMH and corresponding retentions of above 90%. The membranes were dried out over a period of two weeks to determine whether dry storage was possible, and tested again under the same conditions (Fig. 3.3). The results showed reduction in 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 remained low. From this it appears that the membranes should be stored in water before being potted in modules and should not be dried out for prolonged periods of time.

3.3.3.3 *FURFURYL ALCOHOL/ISOPROPANOL MEMBRANES*

Fig. 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.

3.3.4 DISCUSSION

The best-performing membranes were selected for manufacture on a larger scale. It was decided to manufacture the N1X1 (HOIPS), CAMOH 5 and CAMPIP 3 membranes. Enough membranes for eight

1,2 m-long modules were required. Random batches of the membranes would be retested to determine whether the manufacture on a larger scale would be successful. The membranes were stored in a weak, aqueous formaldehyde solution prior to sending them to Membratek.

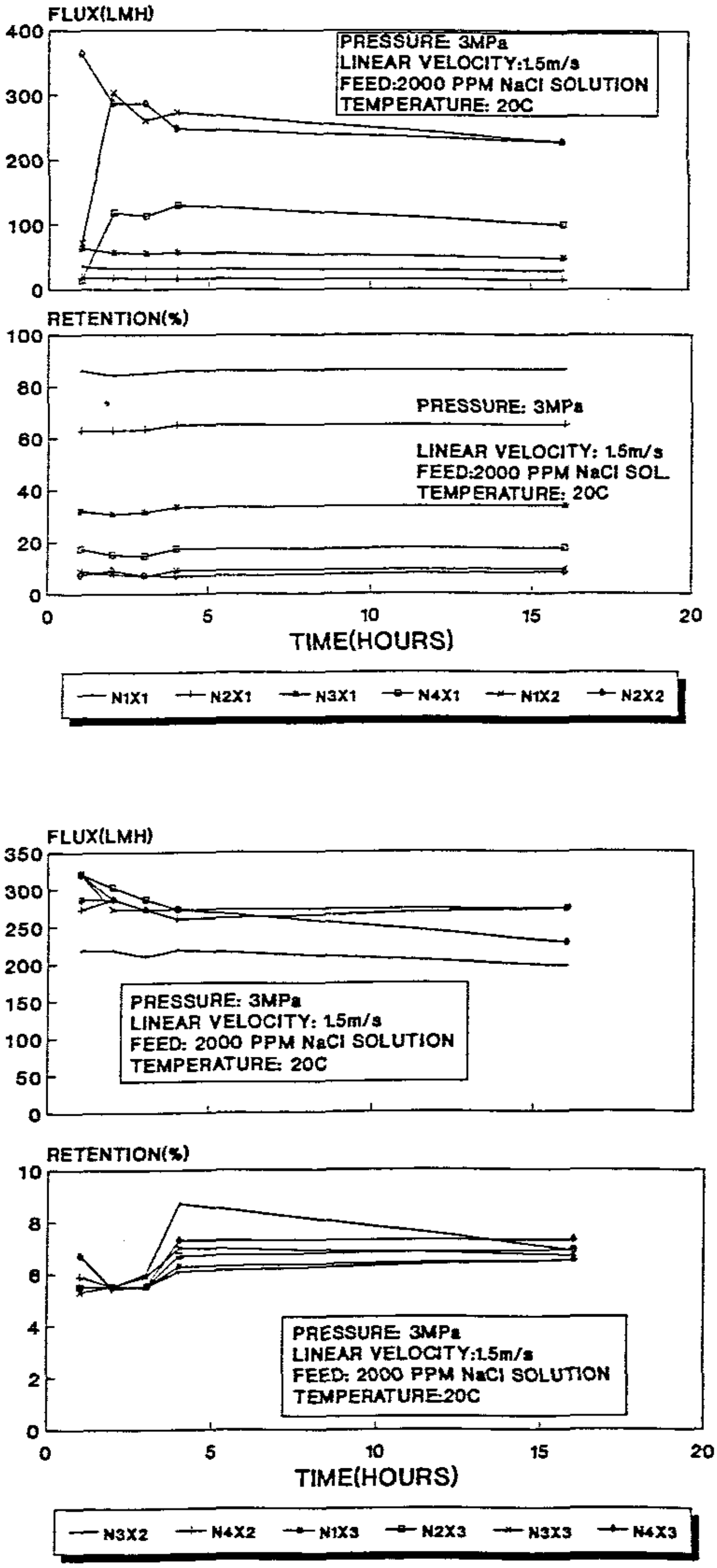


Fig. 3.1:

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

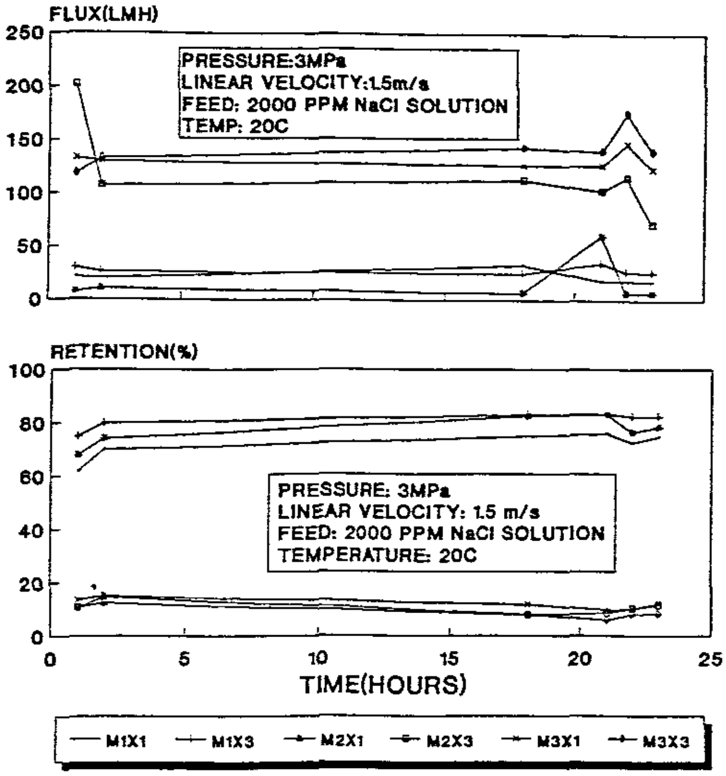


Fig. 3.1:(continues)

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

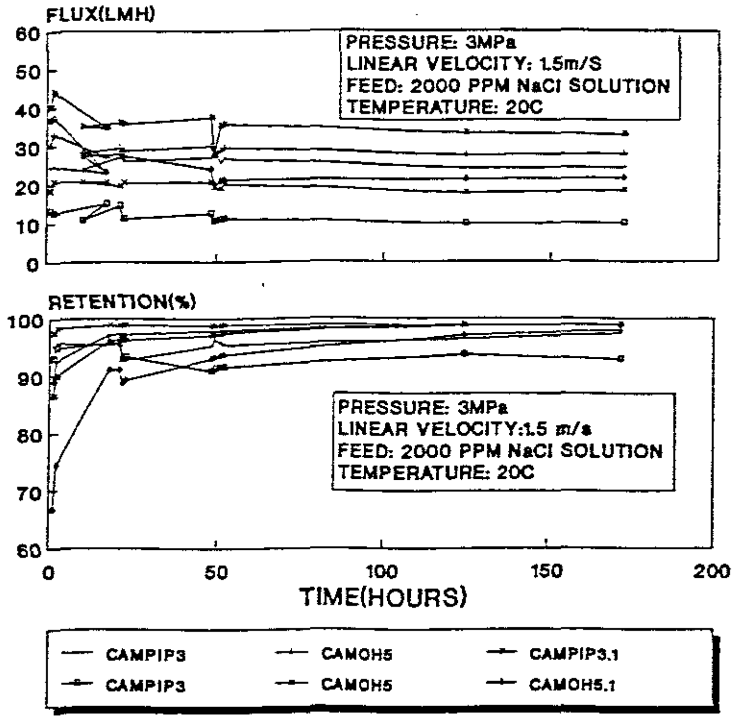


Fig. 3.2:

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

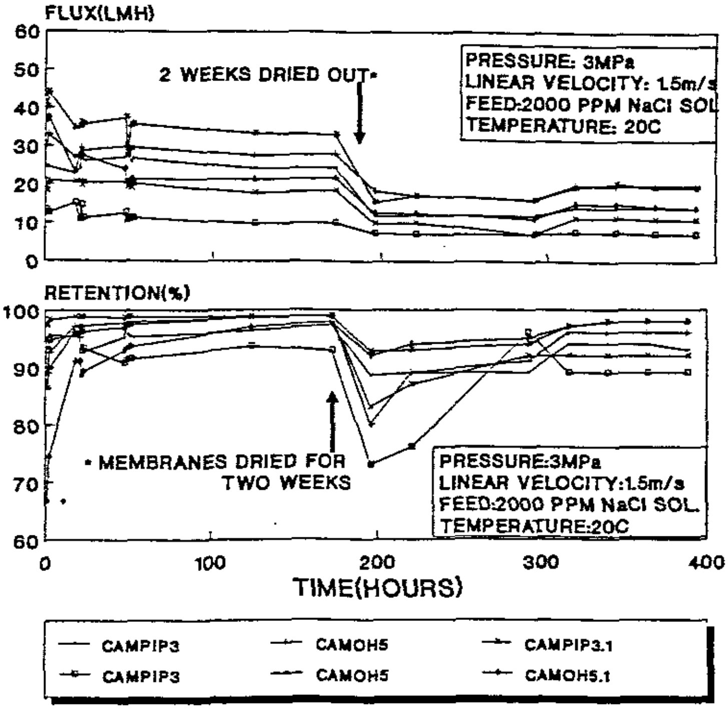


Fig. 3.3:
Flux and retention performance of CAMOH and CAMPIP membranes tested on a 2 000 ppm NaCl feed solution after allowing the membranes to be dried out for two weeks.

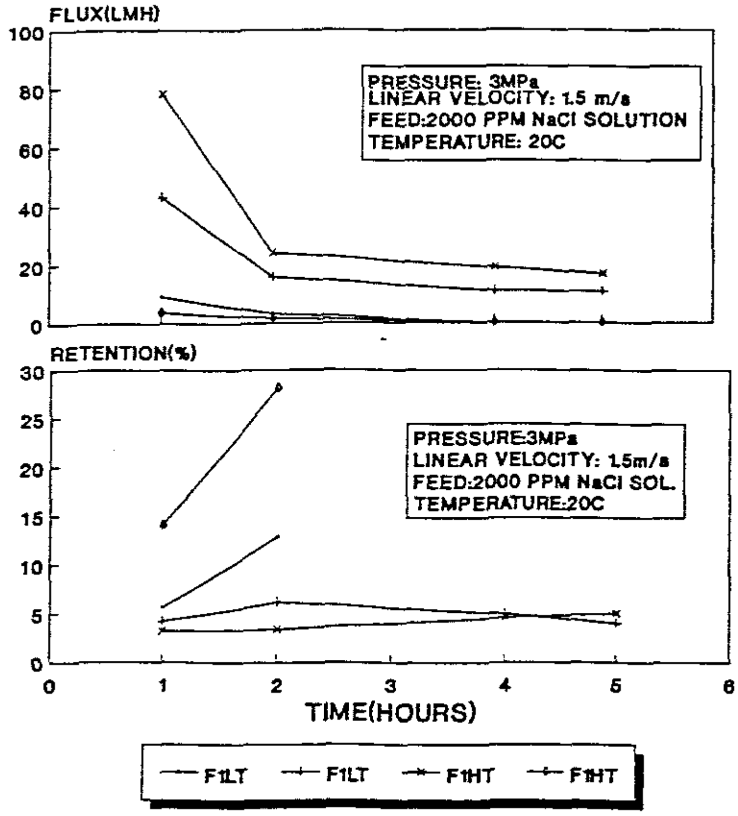


Fig. 3.4:
Flux and retention performance of FURFURYL ALCOHOL/ISOPROPANOL membranes tested on a 2 000 ppm NaCl feed solution.

3.4 LARGE-SCALE PRODUCTION OF MEMBRANES AND MODULE-MAKING

The selected membranes were produced on a larger scale with batch testing at regular intervals. Generally, the same test results were obtained as in the previous small-scale experiment with even higher retentions of up to 99% in the case of CAMOH and CAMPIP membranes (Fig. 3.5). The results show that the CAMPIP membrane gave exceptionally high fluxes (average of 65 LMH) with corresponding average retentions of 99%. The membranes were stored in a weak aqueous formaldehyde solution, and again batch-tested after three days in the solution 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.

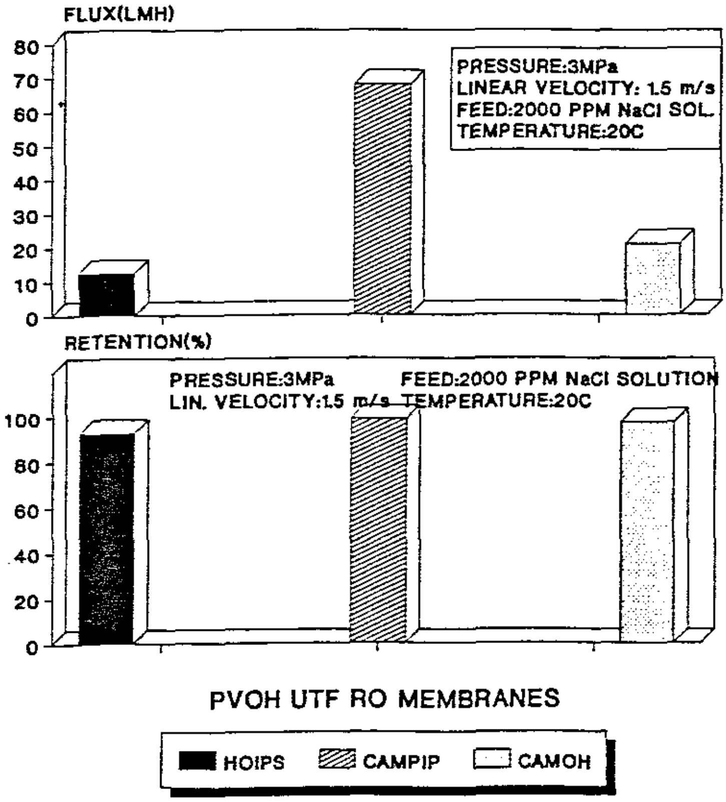


Fig. 3.5:

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 subjected to a standardization test after they had been potted into modules. It was found that both the fluxes of membranes and the retention values had dropped to unaccceptable levels. The modules were sent back to IPS for examination and testing.

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 also 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. The results were compared with the original results collected during membrane fabrication. Figs. 3.6 to 3.8 show only a slight reduction in flux after a drying period of one month. The membranes which were potted in modules, without exception, showed a marked reduction in retention and a corresponding increase in flux.

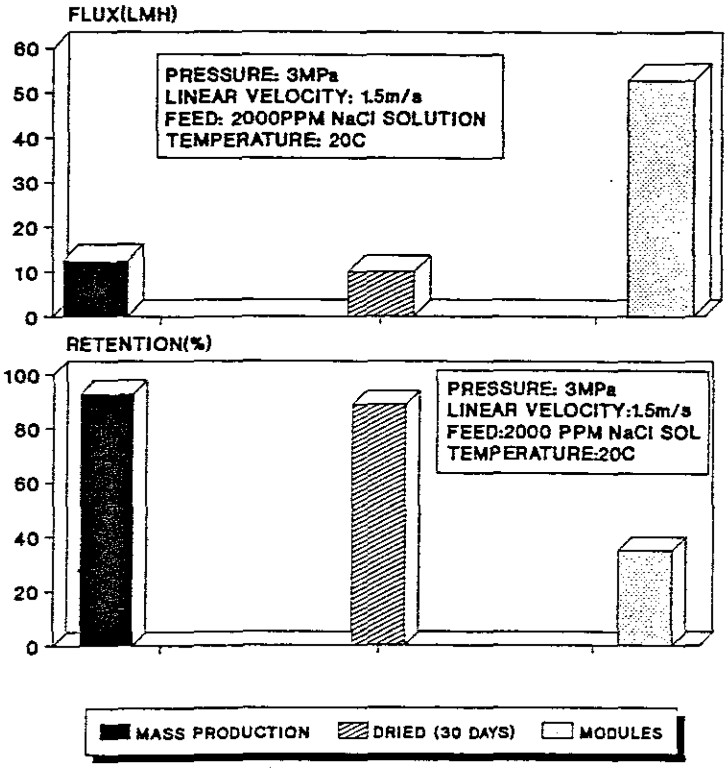


Fig. 3.6:
Comparison of HOIPS membrane performance after: (a) mass production, (b) a drying period of one month, and (c) incorporation into modules.

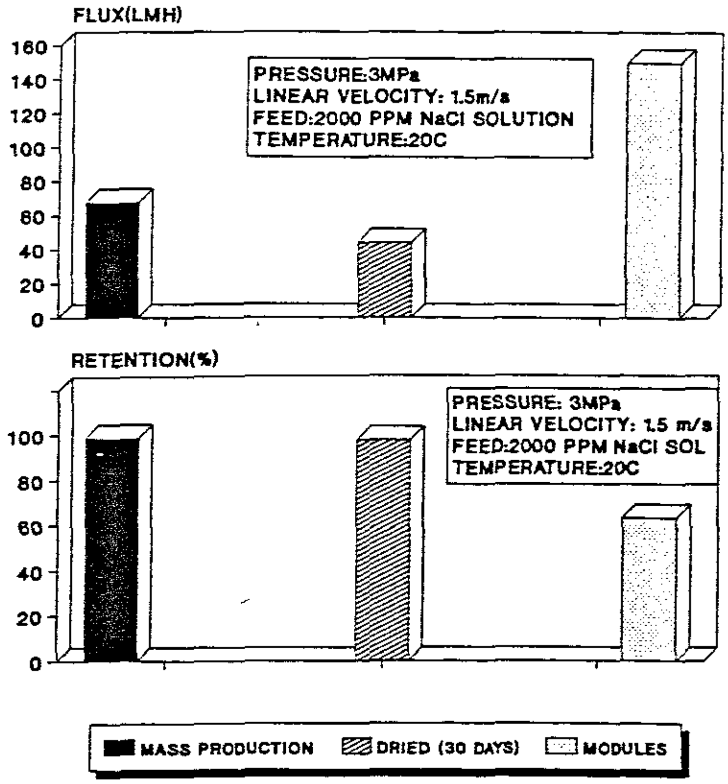


Fig. 3.7:
Comparison of CAMPIP membrane performance after: (a) mass production, (b) a drying period of one month, and (c) incorporation into modules.

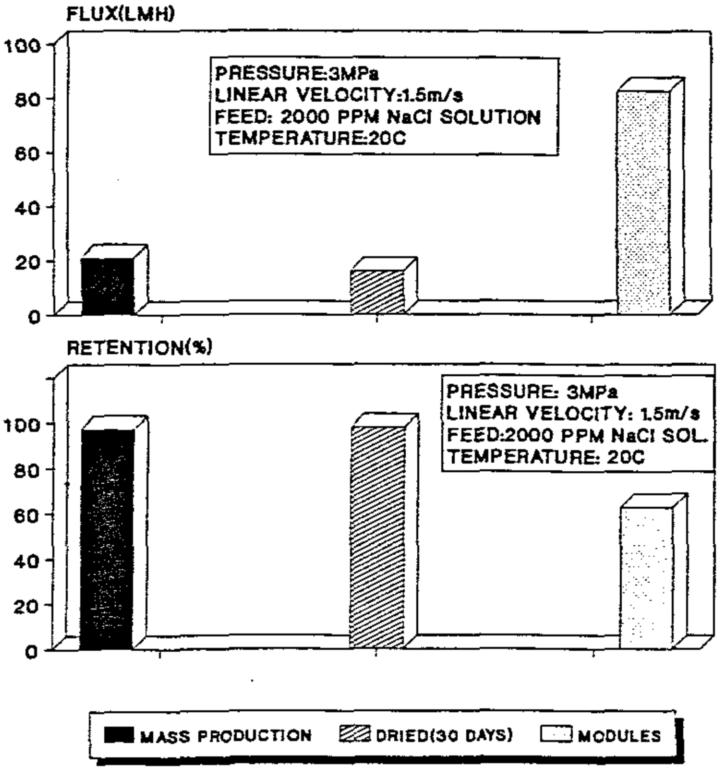


Fig. 3.8:
Comparison of CAMOH membrane performance after: (a) mass production, (b) a drying period of one month, and (c) incorporation into modules.

3.5. CONCLUSIONS

The following may be reasons for the poor performance of membranes after the module-making process:

(i) Unsuitable storing methods during the period before potting.

(ii) It is possible that the membranes dried out to a certain extent during the module-making process. As noted previously, this caused only slight decrease in flux.

(iii) 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 required care and therefore it is 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 testing. However, during the potting process longer lengths of these membranes were handled and therefore the tubes were more susceptible to bending and subsequent damage to the UTF membrane layer.

From the data available it is clear that further research still has to be done to establish methods for storing these UTF-RO membranes. The membranes should be stored for prolonged periods in the formaldehyde solution to determine whether they deteriorate with time. Other possible storing solutions should also be considered.

Ways to minimize damage during module-making should receive the most 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.

CHAPTER 4

MEMBRANE APPLICATIONS ON SASOL COOLING-WATER BLOWDOWN

4.1 INTRODUCTION

When water is re-used in a closed system or otherwise, an inevitable build-up of salt and organic concentrations occurs in the system due to evaporative loss of water for example. Scale formation in equipment is one result of a salt build-up in the system, and fouling of heat exchange surfaces can result from the presence of organic material, dissolved and suspended species. These problems may partly be solved by continuously bleeding off some of the saline (blowdown) water and using it to consolidate ash dumps or by evaporation in ponds, while fresh make-up water is added to the sytem. The disadvantage of the latter method is the high cost of building the dams and also limited space available for the dams.

A solution to the above problem would be either to increase the salinity of the stream going to the evaporation dams and ash dumps, or to gradually decrease salt and organic concentrations within the cooling circuit. Pressure-driven membrane operations such as ultrafiltration and reverse osmosis provide a method of achieving this. It was therefore decided to test experimental ultrafiltration and RO membranes on an effluent with particularly high salinity and organic contents.

The quality of the Process Cooling-water (PCW) in the Sasol Two and Three works has 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 variation 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, received high priority.

The greater PCW system is shown in Fig. 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, referred to as fresh API. The main streams out of 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.

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 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 increased by approximately 12% but stabilized in the past two years, probably due to precipitation.

(iii) Total hardness levels have improved in the past two years and are lower than five years ago.

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

It was decided to test UF and RO membranes developed at IPS on SASOL cooling-water blowdown. CWBD was sent regularly to Stellenbosch in 200ℓ drums. Various membranes were tested on this effluent. After extensive testing of tubular UF membranes, capillary UF membranes and PVOH nanofiltration 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.

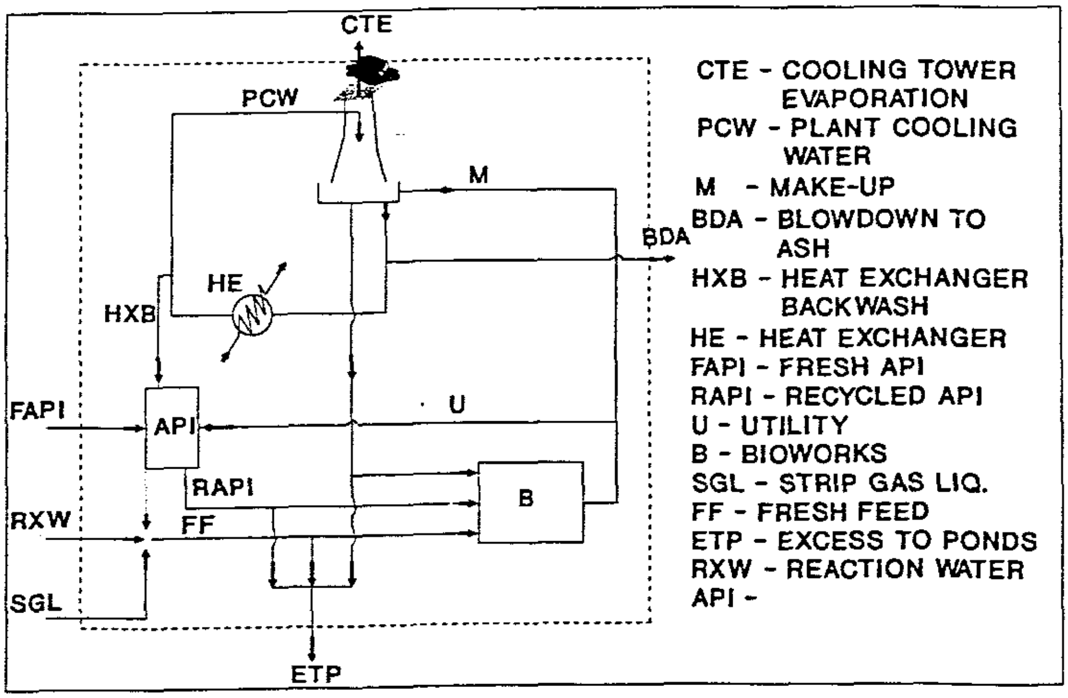


Fig. 4.1:
Process Cooling-Water System.

TABLE 4.1: COMPONENTS IN CWBD WHICH CAUSE PROBLEMS

CONTAMINANT	SYMBOL	FOULING	SCALING	CORROSION
SUSPENDED SOLIDS	SS	■■		
CHEMICAL OXYGEN DEMAND	COD	■■		■
AMMONIA	NH_3	■		■
PHOSPHATE	PO_4^{3-}	■	■	■
FLUORIDE	F^-		■■	
SULPHATE	SO_4^{2-}		■	■■
CALCIUM	Ca^{2+}		■■	
CHLORIDE	Cl^-			■
SILICA	SiO_2		■■	
ALUMINA	Al_2O_3		■■	

■■ = Major influence

■ = Minor influence

4.2 OBJECTIVES

These were to:

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

(ii) test and evaluate ultrafiltration membranes on CWBD as a posssible means for pretreatment prior to reverse osmosis;

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

(iv) test experimental UF capillary membranes;

(v) determine problem areas associated with membrane application;

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

4.3 BACKGROUND

Examples of boiler water and power plant make-up water treatment with reverse osmosis do exist in literature [Ref. 4.1, 4.2, 4.3, and 4.4]. However, few examples of cooling water blowdown treatment with membrane processes exist. In a study conducted by Kostrikin et al., RO was proven to be ecologically the safest technology for make-up water preparation at power plants when comparing it to ion exchange and thermal desalination (using evaporators) [Ref. 4.5].

Tang et al. reports on the use of UF, RO, and electrodialysis to treat wastewaters at electrical power stations. His studies include the recirculation of condense water, ash sluice water, coal pile drainage, boiler blowdown, make-up treatment wastes, chemical cleaning wastes and wet SO_2 scrubber wastes after treatment with membrane processes [Ref. 4.6].

The preparation of boiler water make-up from cooling tower condensate using RO to remove 95% salts, organic compounds and colloids was reported by Brunner [Ref. 4.7].

A pilot study utilizing tubular reverse osmosis (TRO) as a means of desalinating cooling-water blowdown was successfully carried out at Grootvlei Power Station (RSA) during 1984. A 30 m^3/day TRO pilot plant consisting of 30 modules was evaluated over a period of 4100 hours. The study confirmed that the locally developed TRO system could effectively desalinate cooling water blowdown for re-use in a power station, thereby eliminating discharge of high TDS water (see Table 4.2) [Ref. 4.8]. Following this study, a 9 Mℓ TRO plant was constructed at Lethabo [Ref. 4.9] and is currently one of the largest plants of its kind in the world. This plant was designed to treat 9 Mℓ/day of cooling-water at a concentration of 1 300 mg/ℓ TDS with a 70% product recovery and 90% salt retention. This means that approximately 10 tons of salt would be removed from the cooling circuit daily [Ref. 4.10].

TABLE 4.2: FEED, PERMEATE AND REJECT QUALITY AND CONDITIONS AT LETHABO POWER STATION

DESCRIPTION	FEED	PERMEATE	REJECT
Flow m^3/h	375	263	112
Temperature °C	25-30		
pH	4,5-5,5	5,4	5,0
Calcium as Ca^{2+}	108	3	360
Magnesium as Mg^{2+}	14	1	63
Bicarbonate as HCO_3^-	61	Nil	Nil
Chloride as Cl^-	229	23	763
Sulphate as SO_4^{2-}	576	21	2080
Sodium as Na^+	286	30	60
Silica as SiO_2	20	3	60
TDS	1 300 max	81	4 276
Water recovery %		70	

All values in mg/ℓ unless otherwise specified.

Treatment of cooling-water make-up and also cooling-water blowdown had been investigated at Secunda by means of a TRO system. The membranes used in the system were of the cellulose acetate (CA) type. Treatment of CWBD resulted in a high degree of fouling of the membranes. Although the fouling was not permanent and was reversible by soap washes, frequent cleaning made it a less attractive alternative. It was clear that either the feed had to be pretreated or a different method of operation such as seeded slurry would have to be used in conjunction with RO [Ref. 4.11].

From the above, it is evident that the CWBDs from two different industries could not necessarily be treated by the same problem-solving technique. The problem of high concentrations of suspended and organic material in Sasol CWBD is unique and also poses a unique fouling problem, when pressure-driven membrane systems are used as a water recovery method. This problem was reinvestigated in the light of newer experimental membranes that became available.

4.4 ULTRAFILTRATION AS METHOD OF PRETREATMENT

4.4.1 WHY ULTRAFILTRATION?

Various industrial effluents have different chemical compositions and therefore behave differently to membrane treatment. In the case of this particular effluent the challenge to recover water using pressure-driven membrane systems to the extent that it meets the desired standards for re-use, 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 soap washes. Use of a UF membrane which exhibits greater hydrophilic properties may help to combat fouling.

It should be noted that seasonal fluctuations caused changes in composition and concentration of the batches of effluent received from Sasol. It was therefore decided to have effluent sent to IPS at regular intervals. Table 4.3 shows that the effluent consists of suspended particles, salts and organic substances.

As shown in Table 4.4, 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 for pretreating the effluent prior to RO or other desalting methods.

Tubular ultrafiltration membranes as well as capillary UF membranes were tested on Sasol cooling-water blowdown. The tubular UF membranes included membranes with various cut-off points in the UF range (Table 4.5). At this stage the capillary UF membranes were in a very early stage of development, and were not characterized with regard to molecular mass cut-off (MMCO). (Polyethylene glycol was used to characterize the MMCO of the membranes.)

TABLE 4.3: A TYPICAL ANALYSIS OF PROCESS COOLING-WATER AT SASOL

pH	6,7 - 7,5
Na^+	240 - 750
SO_4^{2-}	760 - 2 200
Cl^-	162 - 517
COD (Total)	924 - 3 092
NH_3	230 - 975
PO_4^{3-}	2,8 - 23
F^-	48 - 485
TDS	1 700 - 5 471
Conductivity	3 268 - 8 150
SiO_2	56 - 225

All values in mg/ℓ except conductivity which is in µS/cm.

TABLE 4.4: UF AND RO FUNCTION

Membrane	Operating Pressure	Function
Ultrafiltration	200 - 500 kPa	Organic + macromolecular removal
Reverse Osmosis	2 - 4 MPa	Salt removal

Ultrafiltration → reduces the fouling potential
Reverse Osmosis → reduces scale-forming potential

TABLE 4.5: MOLECULAR MASS CUT-OFF POINTS OF DIFFERENT TUBULAR UF MEMBRANES

Membrane code	PEG molecular mass
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

Tests conducted by Sasol in the past suggested that the suspended solids and macromolecules present in the effluent inhibit crystal growth of the salt fraction in the effluent to a certain extent and subsequent scale formation on equipment. For this reason it can be argued that through removal of suspended solids and macromolecules alone, an increase in scale formation on equipment (*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 reverse osmosis 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. In doing so, problem areas could be pointed out and possibly rectified.

The advantages of using capillary membranes are:

(i) 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.

4.4.2 DATA ON TUBULAR UF MEMBRANES

4.4.2.1 *TEST CONDITIONS*

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

4.4.2.2 *MEMBRANES TESTED AT 0% RECOVERY*

Ultrafiltration tubular membranes, codes 570, 571 and M719 were tested 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 reached, but within 50 h of testing on fresh effluent, the stabilized flux returned to 25 LMH.

Although no conductivity retention was expected, a retention of 2 to 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 abovementioned membranes showed that Ca^{2+} and Fe^{3+} were the cations that were retained. A slight reduction in COD was also visible (Table 4.6).

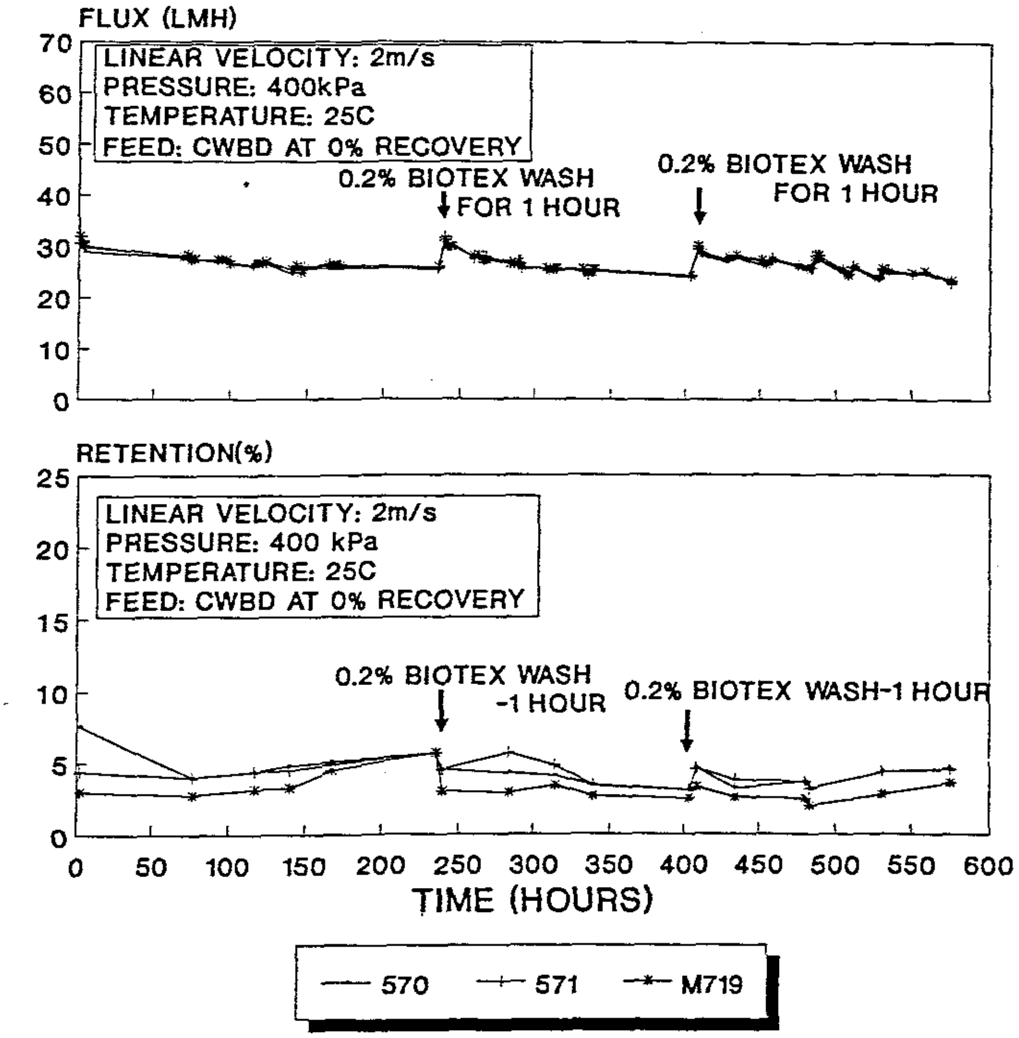


Fig. 4.2:

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

TABLE 4.6: ANALYSIS OF FEEDWATER AND PERMEATE OF DIFFERENT UF MEMBRANES OPERATED ON CWBD AT 0% RECOVERY.

ALL RESULTS IN mg/ℓ							
Cl^-	F^-	Na^+	SiO_2	Fe^{3+}	COD	Ca^{2+}	TURBIDITY
FEEDWATER ANALYSIS							
490	530	723,8	160	9,6	2650	20,7	59
ULTRAFILTRATION MEMBRANE M719							
481	520	720	145	2,9	2080	5,9	3
ULTRAFILTRATION MEMBRANE 570T							
485	510	717,5	160	1,5	2100	5,1	1
ULTRAFILTRATION MEMBRANE 571T							
488	520	695,2	150	1,8	2250	4,5	2

4.4.2.3 *MEMBRANES TESTED AT 20 - 43% RECOVERY*

Ultrafiltration membranes 573, 572, M719, M442, M441 and M440 were tested on SASOL cooling-water blowdown at a product recovery of between 20 to 43%. The initial flux of the different membranes varied from 35 to 55 LMH. Within 200 h the flux of all membranes stabilized at approximately 25 LMH with a corresponding conductivity retention of 5 to 13% (Fig. 4.3). Membranes of the 719 range stabilized at higher fluxes (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 (after washes).

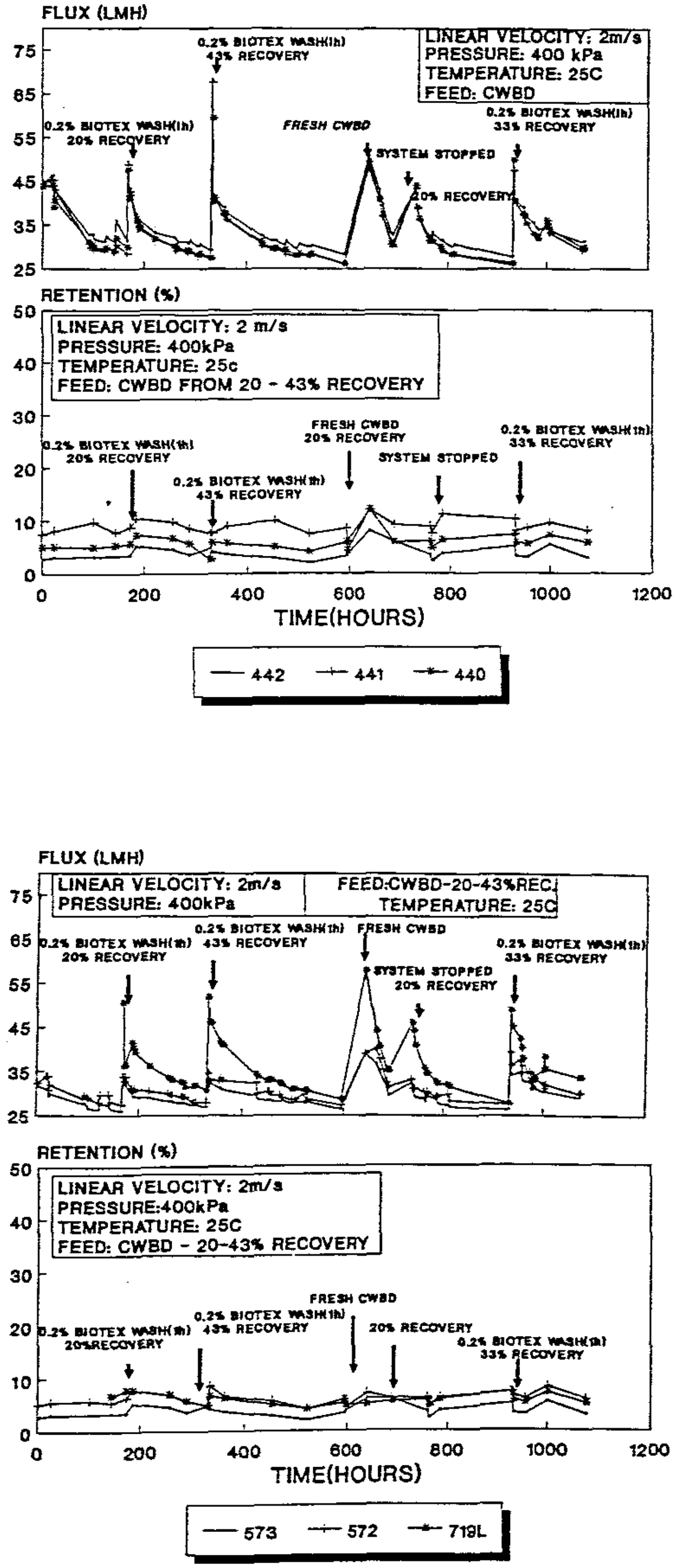


Fig. 4.3:

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

TABLE 4.7: ANALYSIS OF FEEDWATER AND PERMEATE OF DIFFERENT UF MEMBRANES OPERATED ON CWBD AT 20% RECOVERY

ALL RESULTS IN mg/ℓ							
Cl^-	F^-	Na^+	SiO_2	Fe^{3+}	COD	Ca^{2+}	TURBIDITY
FEEDWATER ANALYSIS							
562	565	990,4	160	10	3100	25,2	59
ULTRAFILTRATION MEMBRANE 719							
530	560	742,8	155	2,2	1900	4,5	3
ULTRAFILTRATION MEMBRANE 440							
562	560	780	150	1,5	2500	5,8	0
ULTRAFILTRATION MEMBRANE 441							
534	560	828,5	150	1	1800	6,4	1
ULTRAFILTRATION MEMBRANE 442							
557	563	752,3	160	0,9	1850	5,1	0
ULTRAFILTRATION MEMBRANE 572T							
544	560	717,2	155	2,7	2550	4,5	1
ULTRAFILTRATION MEMBRANE 573T							
534	550	767	160	1,4	2600	7,1	2

Analysis of the CWBD feedwater at 20% recovery and UF permeate showed that up to 75% Ca^{2+} and 50% Fe^{3+} were removed. Slight COD retentions also occurred, although it varied from one membrane to another. As expected with most UF membranes, there was almost 100% colour removal. Cl^-, F^-, Na^+ and SiO_2 levels stayed virtually the same (Table 4.7). Although higher retentions in the case of the lower 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.

4.4.2.4 *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 ultrafiltration stage and thus lessen the burden on the salt removal stage;

(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 ultrafiltration membranes. Disappointing results were, however, obtained when 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.

4.4.2.5 *EFFECT OF pH ON MEMBRANE PERFORMANCE*

A study was also conducted on membrane performance with variation in pH. 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 (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.

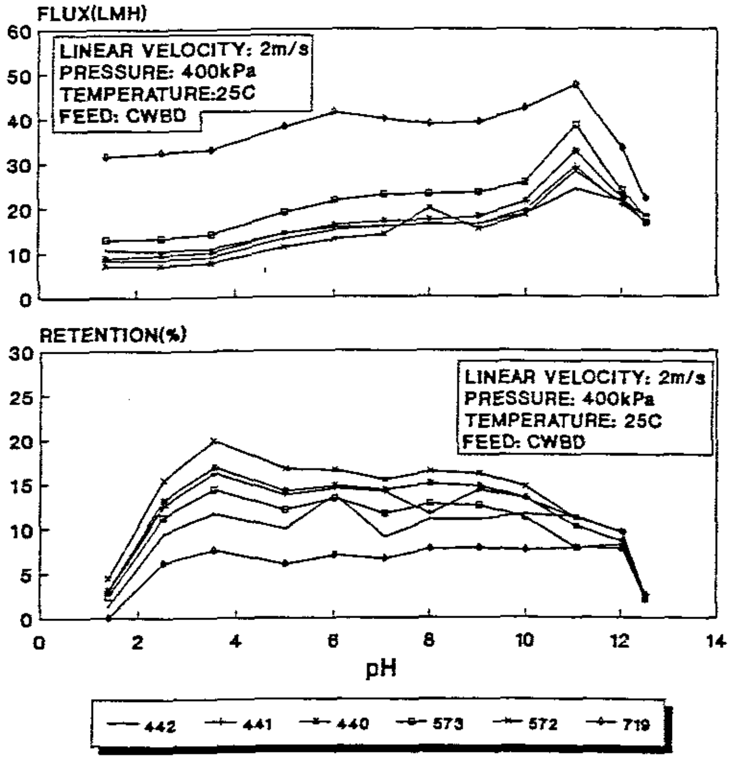


Fig. 4.4:

Performances of different tubular UF membranes to investigate the effect of pH on flux and retention.

4.4.3 CAPILLARY UF MEMBRANES

4.4.3.1. *CHEMICAL RESISTANCE OF EPOXY USED FOR POTTING OF CAPILLARY MEMBRANES IN MODULES*

Capillary membranes were potted in modules with a Ciba Geigy epoxy (Code LY 556).

After 144 h of operation on Sasol cooling-water blowdown, the module developed a serious leak. Stress cracks were discovered at the membrane-epoxy interface, probably caused by the poor elasticity of the epoxy or because of solvent induced stress cracking (Fig. 4.5).

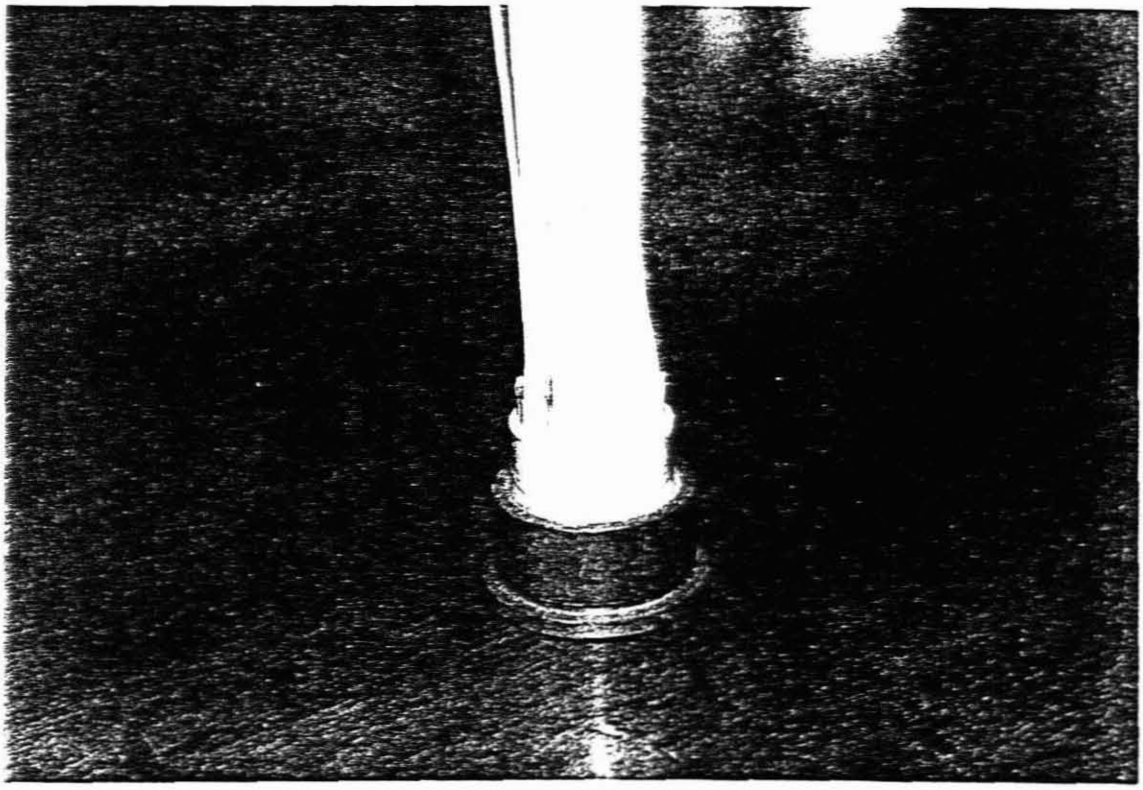


Fig 4.5:
Stress-cracking at capillary membrane base.

It was clear that epoxy LY 556 was not suitable for this application. It was suggested that the LY 556 epoxy's lack of elasticity was the cause for cracking caused by lateral vibration of the capillary membrane during operation. Capillary membranes were then coated with three different epoxies, namely, LY 556, Membralok#1 and Membralok#2. (The latter two epoxies are more elastic than LY 556 and were therefore selected as possible sealants.) The coated capillaries were then placed in Sasol cooling-water blowdown for 24 h. After testing the coated membranes it became evident that the LY 556 epoxy did not have the desired elasticity. The elasticity of the Membralok#1 epoxy was much better, and modules potted with this epoxy showed superior mechanical properties in comparison with LY 556. (Another advantage of the Membralok#1 epoxy was better bonding between the epoxy and the PVC module material.)

To determine the chemical resistance of the Membralok#1, epoxy disks were cast and placed in Sasol cooling-water blowdown for 3 days to investigate the behaviour of the epoxy. Table 4.8 shows that there was no significant increase in the mass of epoxy samples. This shows that no swelling of the epoxy occurred. On inspecting the samples, no solvent stress-cracking was evident, and therefore its suitability as an end-capping material for modules to be tested on CWBD proved satisfactory.

TABLE 4.8: EPOXY EVALUATION - CWBD IMMERSION EXPERIMENT

Sample no.	Weight before immersion (g)	24 h	48 h	76 h
1	6,4101	6,4101	6,4102	6,4102
2	10,5661	10,5670	10,5671	10,5672
3	8,4402	8,4403	8,4403	8,4404
4	9,8712	9,8713	9,8713	9,8714
5	8,1801	8,1803	8,1804	8,1804
Average increase in weight over 3 days		:	0,00018 g	
		=	2,0705 x 10^{-3}% mass increase	

4.4.3.2 *TEST CONDITIONS*

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

4.4.3.3 *TEST RESULTS*

As shown in Figure 4.6, the flux of the capillary module stabilized at 10 LMH with a corresponding conductivity retention of 5%. One of the reasons for the relatively poor flux was the blocking 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, e.g. enzymatic detergent washes and backwashing.

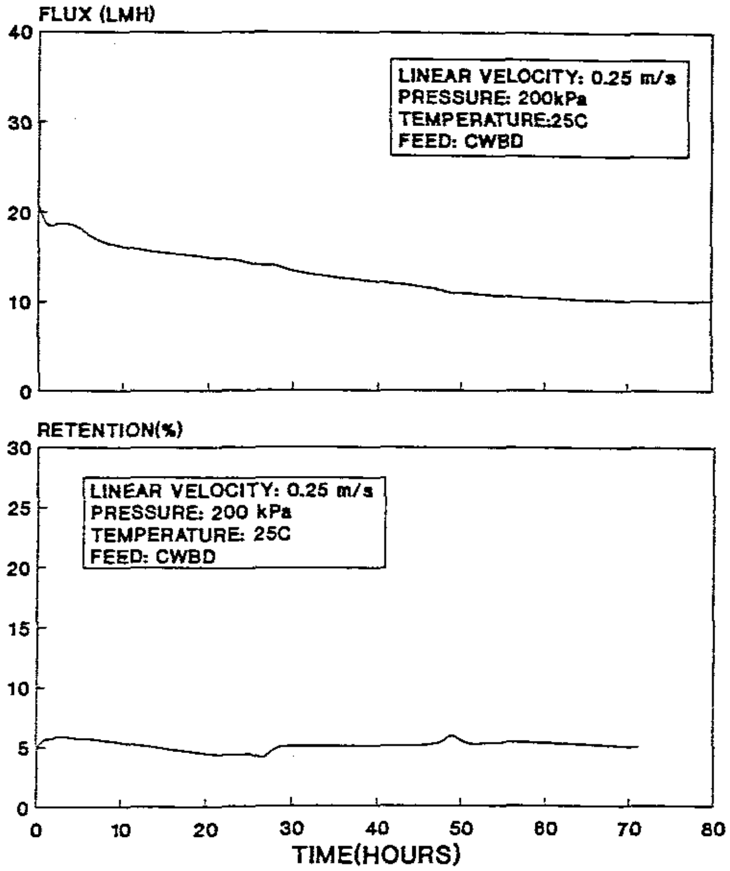


Fig. 4.6:

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

4.5 TUBULAR NANOFILTRATION

4.5.1 BACKGROUND

A robust PVOH nanofiltration membrane was developed. This membrane system offered the following advantages:

(i) dry storage (i.e. wet-dry cycling);
(ii) wide operating pH range;
(iii) not easily oxidized;
(iv) robustness

These membranes were tested beforehand on a 1 000 ppm NaCl solution, as well as on a $MgSO_4$ solution of the same concentration. The results obtained were typical of a nanofiltration membrane. In the case of the NaCl solution, a flux of 80 LMH with corresponding retention of 40% was reached, while a flux of 35 LMH and corresponding retention of 85,9% was obtained in the case of the $MgSO_4$ feed 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 by subjecting it to extensive testing on an oversaturated $CaSO_4$ slurry. The feed consisted of 10 000 ppm $CaSO_4$ and since the solubility of $CaSO_4$ is approximately 2,8 g/ℓ, the feed contained approximately 7,2 g/ℓ undissolved solids.

4.5.2 TUBULAR PVOH NANOFILTRATION MEMBRANE PERFORMANCE

4.5.2.1 *$CASO_4$ SLURRY TEST*

Test Conditions

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

Test Results

Figures 4.7 shows the $CaSO_4$ permeate flux and retention values against 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%).

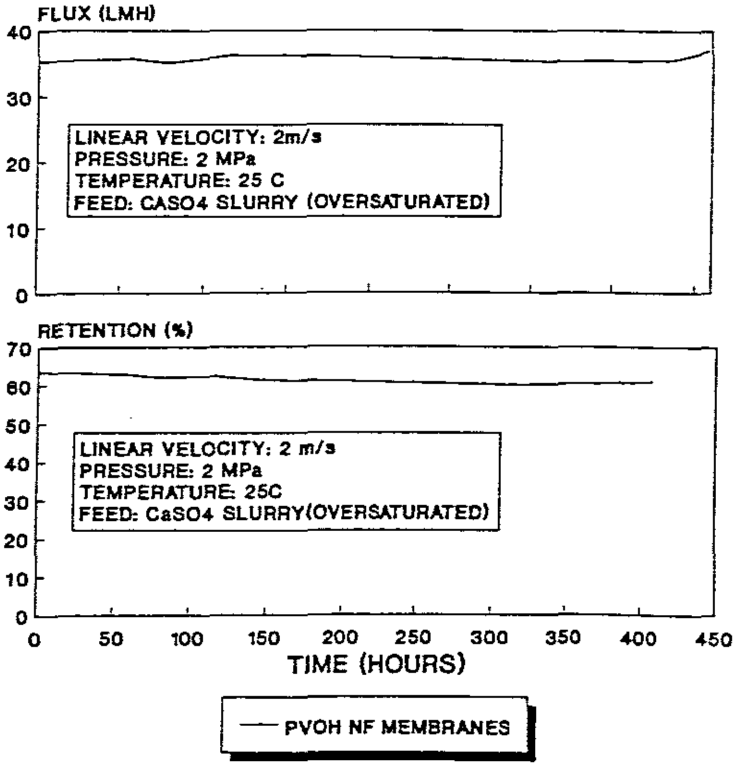


Fig. 4.7:

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

4.5.2.2 *MEMBRANES TESTED 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 (Fig. 4.8) with regard to flux and retention. Stabilized fluxes varied from 15 to 25 LMH with corresponding conductivity retentions of 40 to 75%. Analysis of the permeate showed that 99% of all organic substances had been removed. This showed that a major percentage of the conductivity retention could be regarded as organic retention. These results were typical of a nanofiltration membrane. Each membrane tested was manufactured under different conditions and with different recipes and therefore a difference in membrane performance is evident in the test results. Only the best performing membranes were considered for further development and testing.

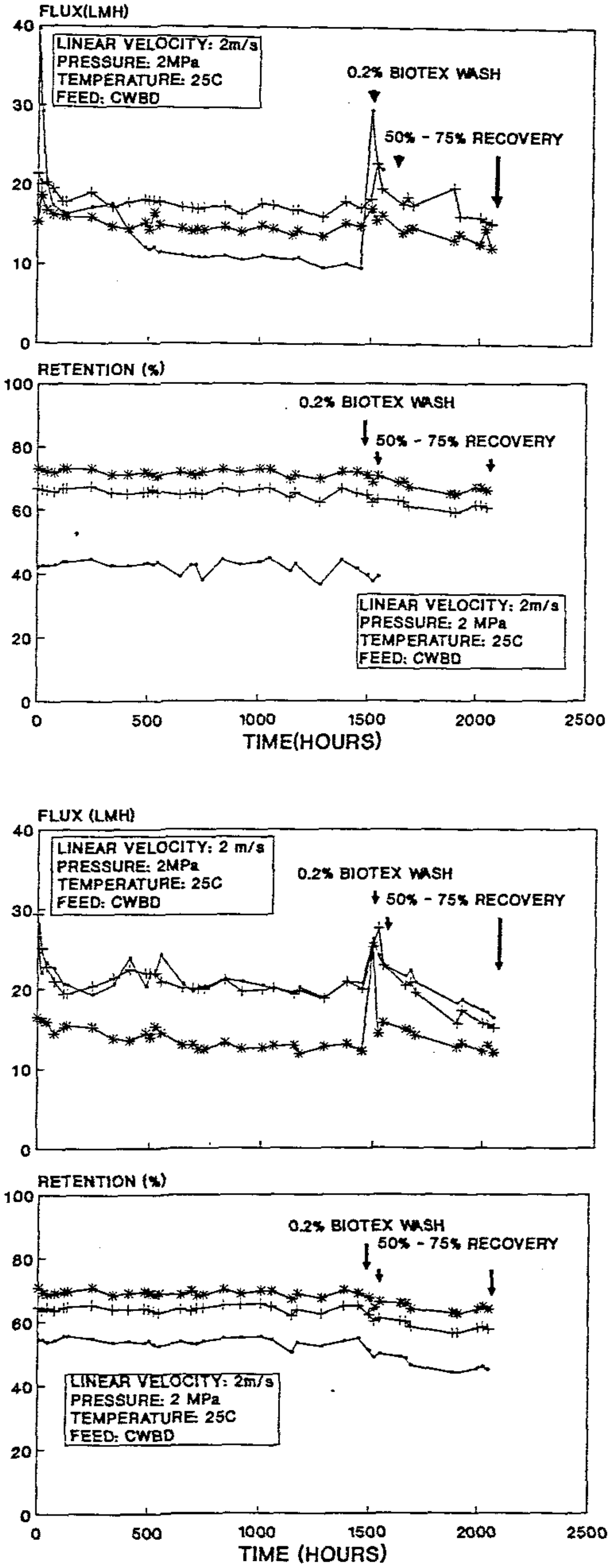


Fig. 4.8:

Flux and retention performances of six different PVOH NF membranes operated on CWBD.

4.6 INSTALLATION OF ON-SITE TEST FACILITIES

4.6.1 PLANNING

It was decided that for SASOL CWBD treatment, two approaches could be followed:

(i) UF as pretreatment to RO;
(ii) Direct application of RO and nanofiltration (an experimental PVOH nanofiltration membrane was available).

Ideally, a salt retention of between 40 to 90% is required in the case of the nanofiltration membrane with a corresponding flux of 30 to 40 LMH. PVOH membranes of high and lower salt retentions had to be tested directly on CWBD.

While new experimental tubular UF membranes had to be tested, high-flux capillary membranes (UF) were also under development to make the pretreatment process viable.

In the light of the above decisions, it was decided to construct three test units which could be used for on-site testing.

4.6.2 DESIGN OF TEST EQUIPMENT

Three test-rigs had to be designed and constructed:

(a) Capillary UF membrane test-rig (Fig. 4.9);

(b) Tubular UF membrane test-rig (Fig. 4.11);

(c) Tubular RO membrane test-rig (Fig. 4.12).

4.6.2.1 *CAPILLARY UF MEMBRANE TEST-RIG DESIGN*

Below follows the design of the capillary membrane testrig (Fig. 4.9).

Assumptions:

(1) Assume 200 capillary membranes per module;

(2) Average capillary ID = 0,0014 m (1,4 mm);

(3) Linear velocity required through capillaries = 1 m/s.

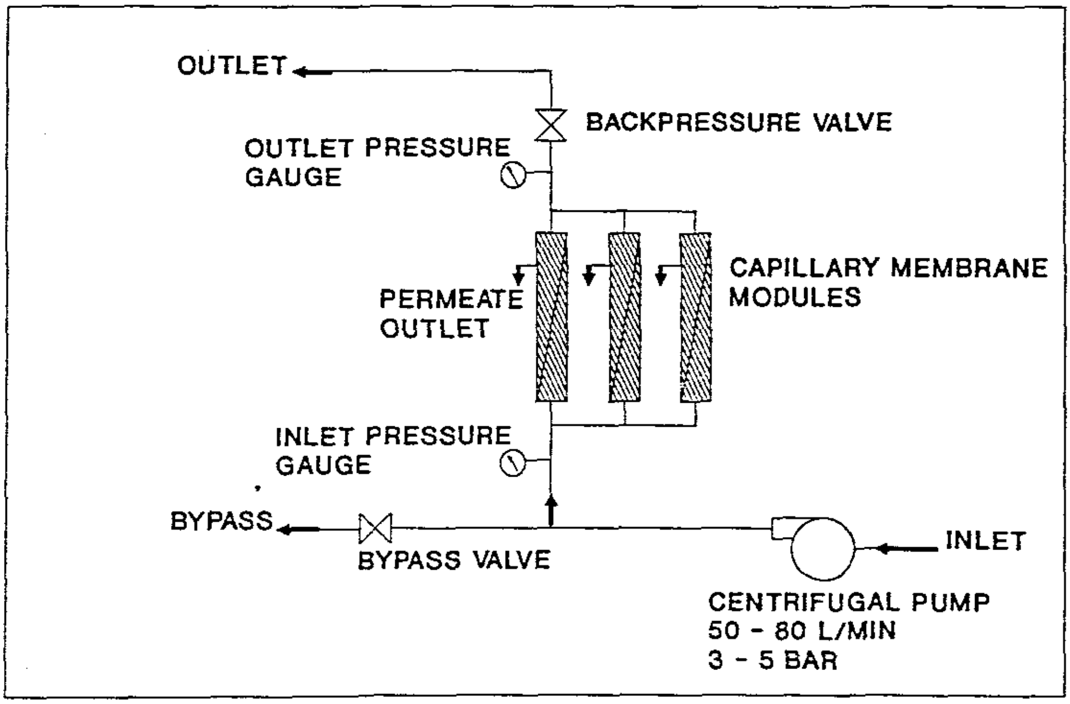


Fig. 4.9:
Capillary UF membrane test-rig design.

$$Q = vA \times N_t \times M \qquad \text{(Eq. 4.1)}$$

Where:

v = linear velocity (m/s)

Q = Volumetric flowrate (m^3/s)

A = cross-sectional area (m^2)

N_t = total amount of capillary membranes per module

M = number of modules.

$$Q = 1 \times \pi \left[\frac{0,0014}{2}\right]^2 \times 200 \times 3$$

$$= 9,236 \times 10^{-4}\ m^3/s \equiv 55,4\ \ell/\text{min}$$

Head loss due to friction:

$$\Delta h_f = \frac{4\ j_f\ L\ v^2}{d_i\ g} \qquad \text{(Eq. 4.2)}$$

Where:

Dh_f = head loss due to friction

j_f = friction factor

L = total equivalent length (m)

v = linear velocity (m/s)

d_i = inside diameter (m)

g = 9,81 (m/s2)

$$v_{pipe} = \frac{Q}{A} = \frac{9{,}236 \times 10^{-4}}{\pi \left[\frac{0{,}032}{2}\right]^2} = 1{,}1484 \text{ m/s}$$

$$Re = \frac{\rho v d}{\mu} = \frac{1000 \times 1{,}1484 \times 0{,}032}{0{,}001}$$

$$= 36748{,}8 \longrightarrow \text{Turbulent flow}$$

$$\therefore j_{f\ (smooth\ pipe\ -\ turbulent)} = \frac{0{,}0396}{(Re)^{0.25}}$$

$$= 2{,}86 \times 10^{-3}$$

$$L_{equivalent} = 4 \text{ m} + (1 \times \text{ball valves}) + (1 \times 90° \text{ elbows}) + (1 \times \text{T-piece})$$

$$= 4 \text{ m} + [1\ (13 \times d)] + [1\ (32 \times d)] + [1\ (60 \times d)]$$

$$= 4 \text{ m} + (1 \times 13 \times 0{,}032) + (1 \times 32 \times 0{,}032) + (1 \times 60 \times 0{,}032)$$

$$= 10{,}24 \text{ m}$$

From Eq. 4.2:

$$\therefore \Delta h_f = \frac{4\ (2{,}86 \times 10^{-3}) \times 10{,}24\ (1{,}1484)^2}{0{,}032 \times 9{,}81}$$

$$= 0{,}5 \text{ m} \text{ (head loss in piping system)}$$

$$\Delta h_{f\ cap} = \frac{4\ j_f\ L\ (V_{cap})^2}{d_{i\ cap} \times g}$$

p

$$j_{f\,laminar} = \frac{8}{Re} = \frac{8}{1000 \times 1 \times 0{,}0014} \times 0{,}001$$

$$= 5{,}714 \times 10^{-3}$$

$$L = 0{,}5 \text{ m}$$

$$\therefore \Delta h_{f\ cap} = \frac{4 \times (5{,}714 \times 10^{-3}) \times 0{,}5 \times 1^2}{0{,}0014 \times 9{,}81}$$

$$= 0{,}832 \text{ m}$$

Head loss due to expansion into module:

$$\Delta h_e = \frac{(v_1 - v_2)^2}{2\ g} = \frac{(1{,}1484 - 1)^2}{2 \times 9{,}81}$$

$$= 1{,}122 \times 10^{-3} \text{ m (negligible)}$$

Where:

Δh_f = Head loss due to expansion into the module.

v_1 = linear velocity in piping system (m/s)

v_2 = linear velocity after expansion into module

Total friction head loss:

$$\Delta h_{f\ total} = \Delta h_{f\ piping} + \Delta h_{f\ cap} + \Delta h_e$$

$$= 0{,}5 + 0{,}832 + (1{,}122 \times 10^{-3})$$

$$= 1{,}333 \text{ m}$$

$$= 13 \text{ kPa} \longrightarrow$$

Total head required:

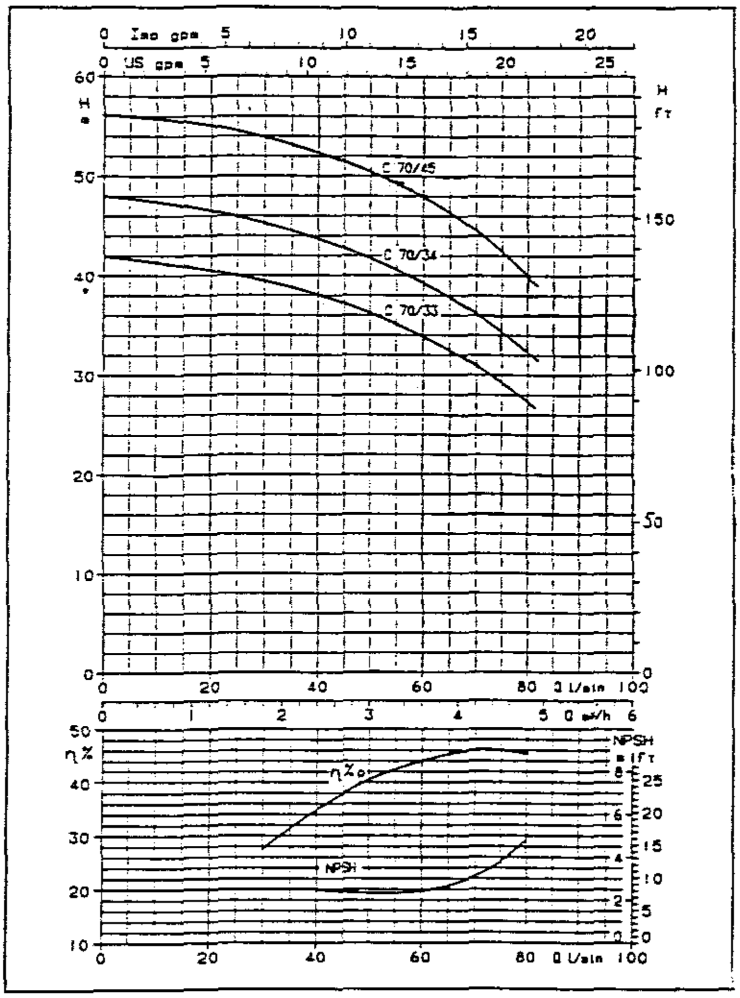
$$= 500 + 13$$

$$= 513 \text{ kPa}$$

∴ Maximum head required = 513 kPa (52 m)

Maximum flowrate Q = 55,4 ℓ/m

It was therefore decided to acquire a Lowara C 70/45 centrifugal pump (see Fig. 4.10).



Courtesy of Flowtech

Fig. 4.10:
Lowara centrifugal pump - pump curves.

4.6.2.2 *TUBULAR UF MEMBRANE TEST-RIG DESIGN:*

Below follows the design of the tubular ultrafiltration membrane testrig (Fig. 4.11).

Assumptions:

(1) Maximum backpressure required = 500 kPa;

(2) Maximum linear velocity required through tubular membranes = 2 m/s;

(3) 12,7 mm (½ ") tubing to be used.

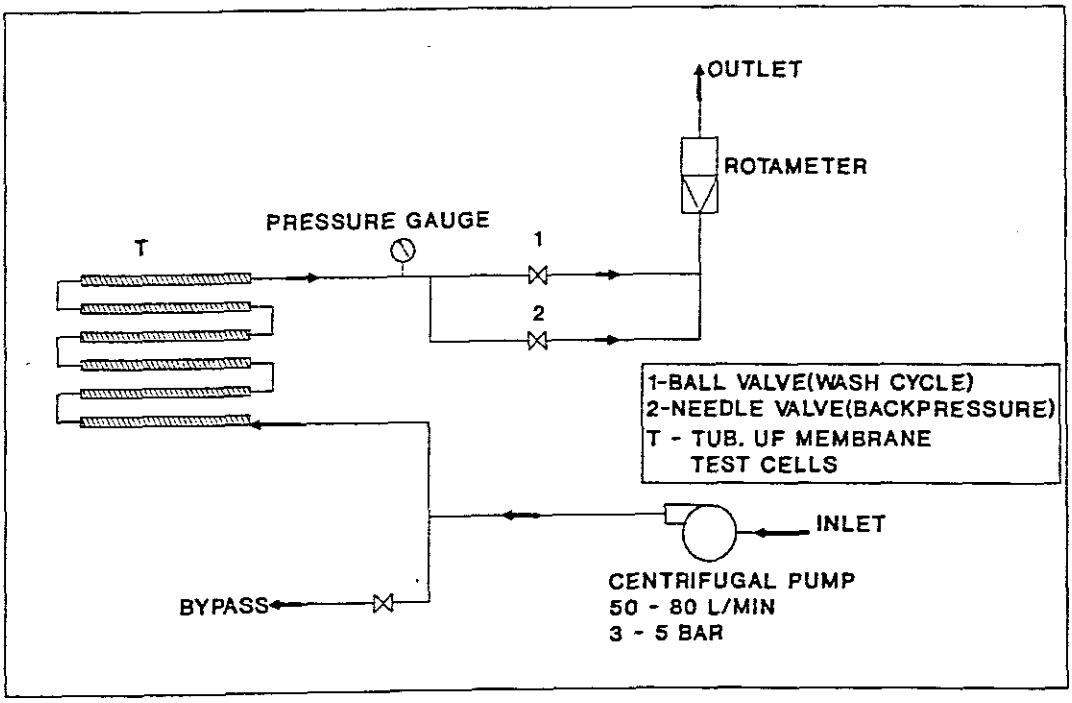


Fig. 4.11:
Tubular UF membrane test-rig design.

$$Q = vA$$

$$= 2 \times \pi \left[\frac{0,027}{2}\right]^2 = 2,533 \times 10^{-4}\ \text{m}^3/\text{s}$$

$$= 912\ \ell/\text{h} \quad (= 15,2\ \ell/\text{min})$$

Head loss due to friction:

$$\Delta h_f = \frac{4\ j_f\ L\ v^2}{d_i\ g}$$

$$Re = \frac{\rho v d}{\mu} = \frac{1000 \times 2 \times 0,0127}{0,001} = 25400$$

$$\longrightarrow \text{Flow is turbulent}$$

$$\frac{\epsilon}{d} = \frac{0,000045}{0,0127} = 3,54 \times 10^{-3}$$

Where ϵ = total pipe roughness (m).

$\therefore$ From pipe friction chart j_f vs Re ⟶ $j_f = 0,004$ [Ref. 4.12]

$$L_{equivalent} = 11\ \text{m} + (14 \times 90^\circ\ \text{elbows}) + (1 \times \text{gate volume})$$

$$= 11 + (14 \times 32 \times 0,0127) + (1 \times 17 \times 0,0127)$$

$$= 16,9\ \text{m}$$

$$\therefore \Delta hf = \frac{4 \times 0,004 \times 16,9 \times 2^2}{0,0127 \times 9,81}$$

$$= 8,681\ \text{m}\ (\equiv 85,165\ \text{kPa})$$

$\therefore$ At a pressure of 500 kPa the total head required is:

$$= 50,96 + 8,68$$

$$= 59,65\ \text{m}$$

According to Figure 4.10 (Lowara pump curve) model C 70/45 is capable of delivering the required volumetric flowrate and head.

4.6.2.3 *TUBULAR RO MEMBRANE TEST-RIG DESIGN:*

PVOH RO membranes to be tested on this test-rig (Fig. 1.12).

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.)

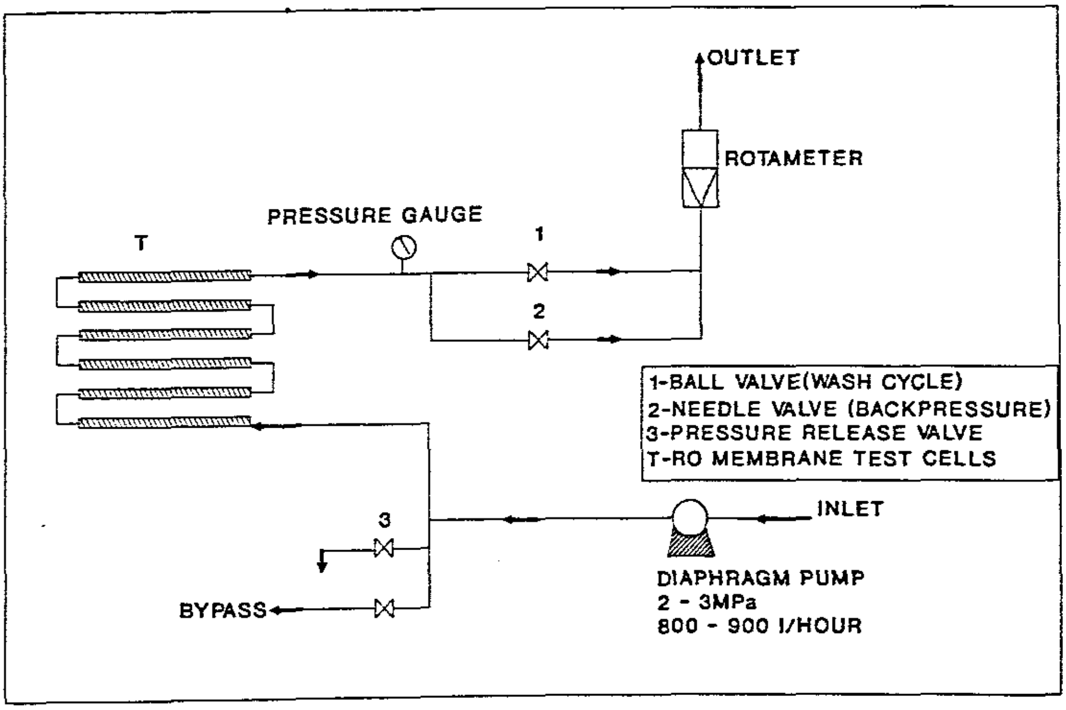


Fig. 4.12:
Tubular RO membrane test-rig design.

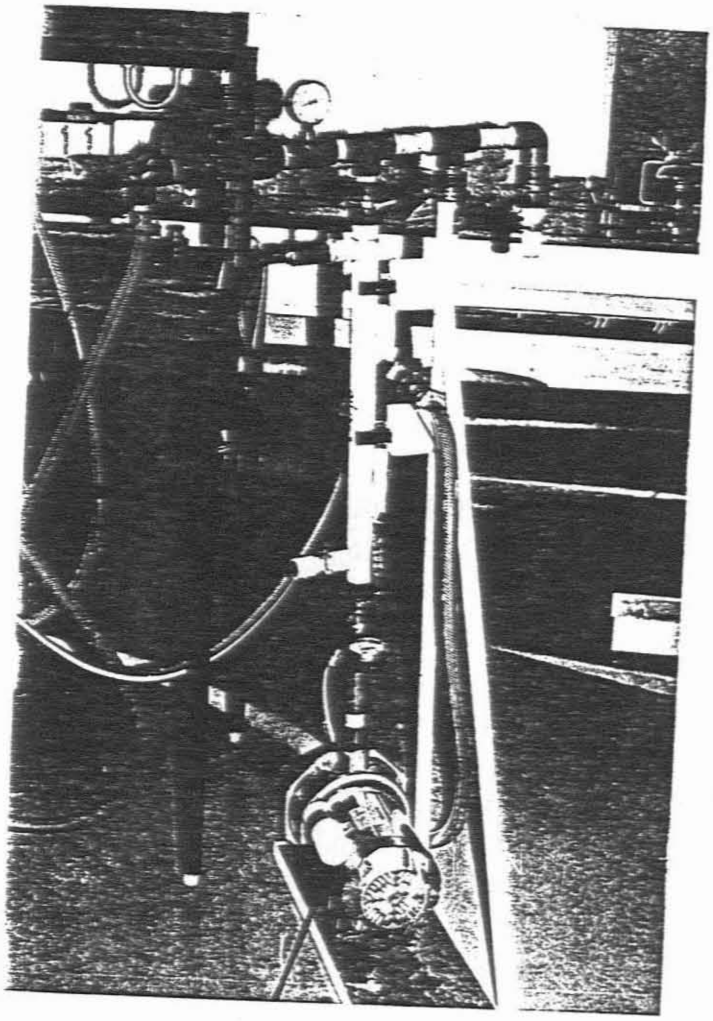


Fig. 4.13:
Capillary UF membrane test-rig

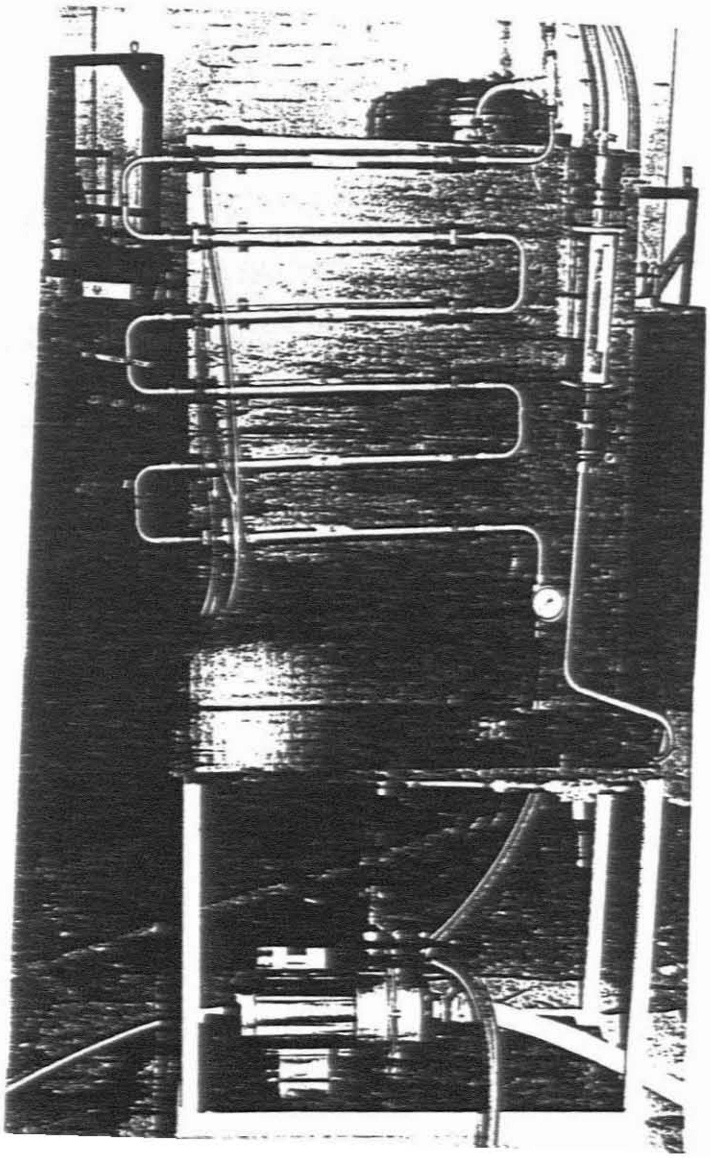


Fig. 4.14:
Tubular UF membrane test-rig.

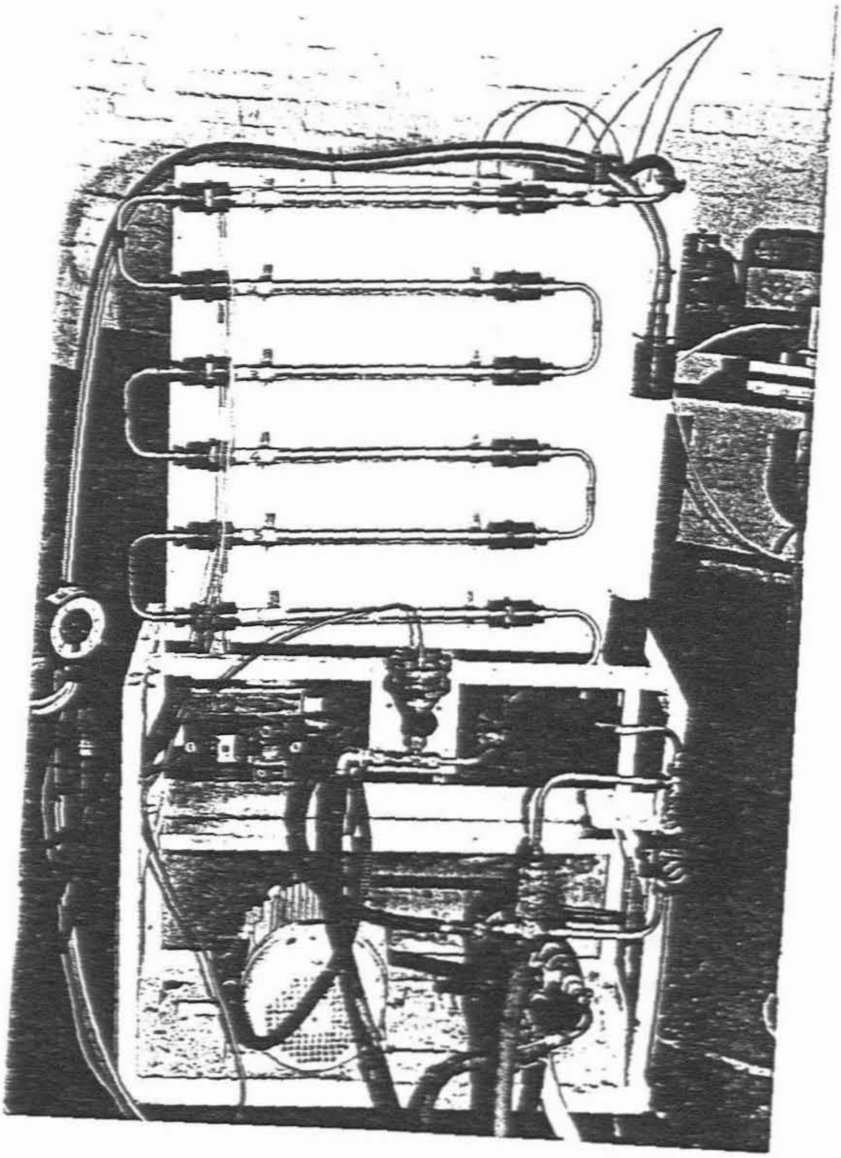


Fig. 4.15:
Tubular RO membrane test-rig.

4.7 ON-SITE MEMBRANE EVALUATION

4.7.1 BACKGROUND

After completion of laboratory scale membrane evaluation studies at IPS, it was decided to install the three test-rigs at Secunda. The next step was to evaluate successful ultrafiltration, nanofiltration and reverse osmosis membranes candidates on fresh effluent.

Because the effluent underwent chemical changes when stored for a period of time, it was of great importance to constantly work on this fresh effluent in order to simulate true conditions during testing. Sasol undertook to maintain and monitor the test equipment and to supply IPS regularly with the relevant test data.

The idea was to test as many experimental tubular UF, capillary UF, nanofiltration and RO membranes as possible. This investigation would provide valuable information regarding the perfomance of these membranes on this specific industrial effluent. The idea was also to test the membranes at increasing concentrations (% recovery) and to determine to what extent these concentrations influenced the performance of the membranes.

4.7.2 TEST RESULTS

4.7.2.1 *TUBULAR ULTRAFILTRATION MEMBRANES*

Batch 1

An experimental batch of UF membranes was installed in the UF test-rig at Secunda. A problem which arose was the need for an effective way of controlling the feed temperature on site. A cooling system to prevent the water from heating due to recirculation was constructed. Tapwater was used as cooling medium, but slight feedwater temperature fluctuations still occurred because of fluctuation in cooling water temperature. Because of the fluctuation in cooling water temperature, a variation in the feedwater temperature of 23 °C to 30 °C caused fluctuations in membrane performance. The membranes (codes: E578T/744, E577/743, M719L, 442, 440) were all experimental with the exception of M719L, which is a well-established commercial UF membrane. Whereas the M719L had a MMCO of 60 000 MM PEG, the experimental membranes had the following PEG MMCOs:

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

Figure 4.16 shows that the flux stabilized (after approximately 50 h) to 20 LMH with a corresponding conductivity retention of 15% to 20%. The high retention was most probably the result of a gel layer which formed on the membrane surface. The variations in permeate flux and retention were the results of changes in chemical composition of the effluent and variation in the feed-water temperature. After

1 200 h of operation a 0,2% soap wash was done. A rapid increase in flux to about 50 LMH showed that the membrane had not been permanently fouled. The test was performed at 0% recovery.

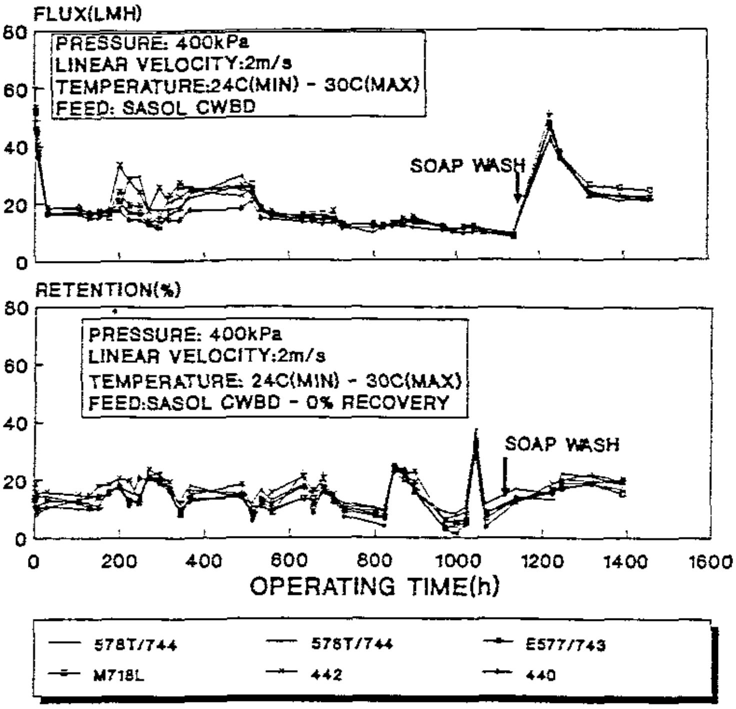


Fig. 4.16 :

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

Batch 2

New experimental UF tubular membranes, namely, 440, 442, 572, 572, 573 and 574 with different MMCOs, were installed. A commercial M719L UF membrane was also installed as control. The PEG MMCOs for the experimental membranes were:

440 - 6 000 dalton

442 - 6 000 dalton

572 - 6 000 dalton

573 - 35 000 dalton

574 - 25 000 dalton

A pure-water flux test was first done (Fig. 4.17), and then followed by a test run of 75 h on CWBD at 0% recovery. A range of tests at different concentrations (recoveries) were started with a 0,2% soap wash preceding 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 (Fig. 4.18).

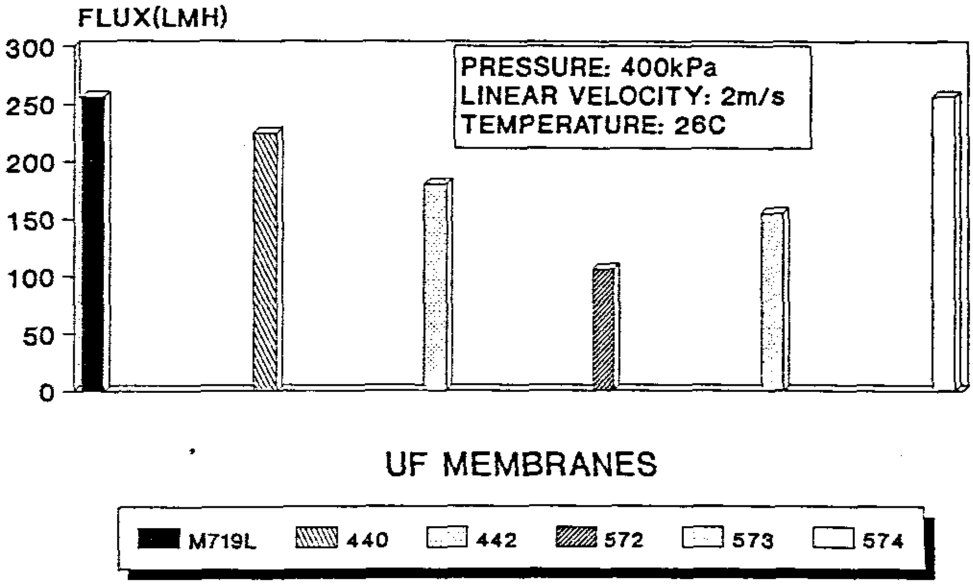


Fig. 4.17:
Pure-water flux - Tubular UF membranes.

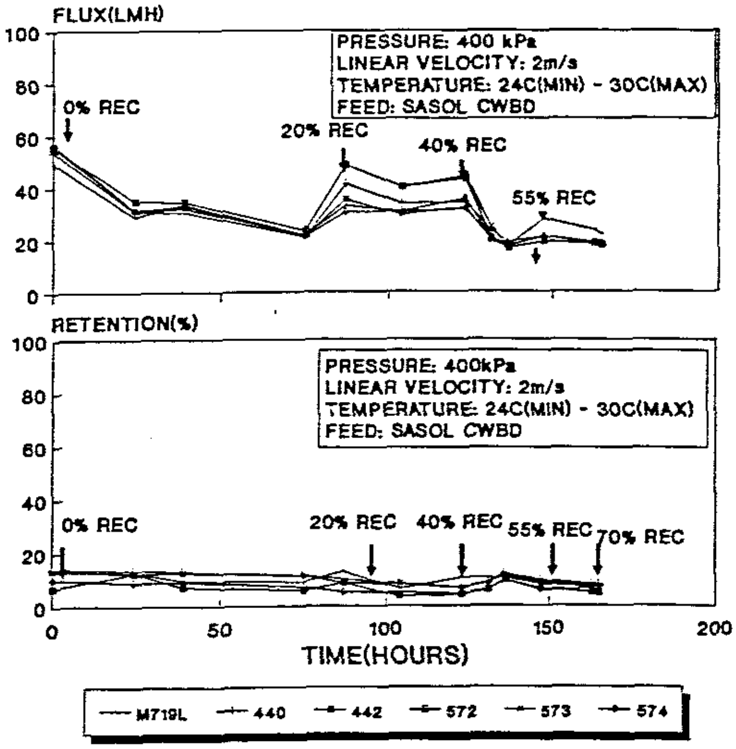


Fig. 4.18:
Flux and retention performances of six sets of different tubular UF membranes operated on CWBD at different recoveries.

Figure 4.19 shows a marked decrease in flux with an increase in concentration. A slight drop in retention is also observed in the plot of retention against percentage recovery.

Analysis of the UF permeate showed, surprisingly, a reduction of 20% $CaSO_4$ (average for all UF membranes tested). The colour retention was 99% and the COD retention between 20% and 25%. The high colour retention was expected because UF membranes retain macromolecules. The reductions in COD and $CaSO_4$ concentrations were most probably the results of gel-layer formation on the membrane surface.

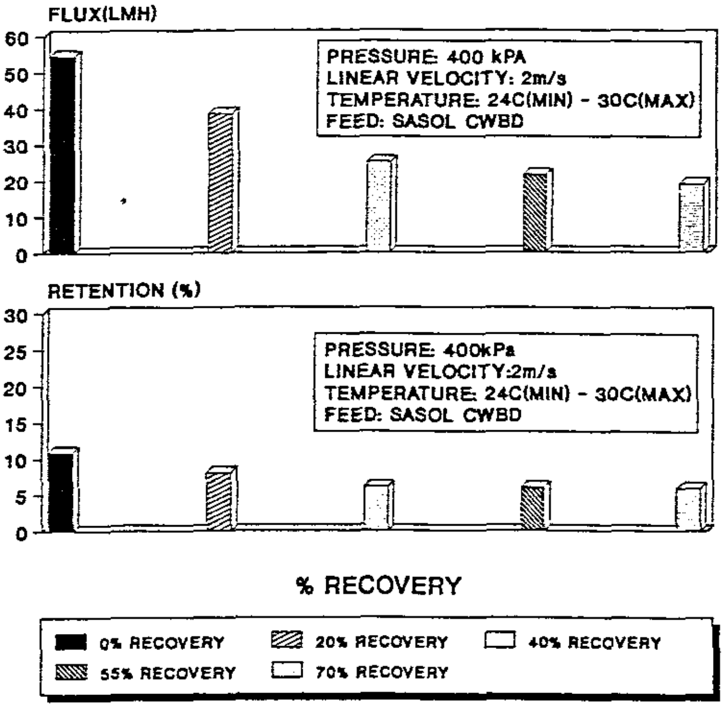


Fig. 4.19:

Flux and retention performances of different tubular UF membranes when plotted against different concentrations (recoveries) of CWBD.

4.7.2.2 *CAPILLARY ULTRAFILTRATION MEMBRANES*

Two experimental capillary UF modules were tested on the effluent. The advantage of these membranes is their higher packing density (when compared with tubular membranes) and lower operating pressure (200 kPa). However, problems were 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 1 000 micron filter ahead of the capillary membrane operation. Bridging (see Fig. 4.20) 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 lies most probably 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 on inspection during and after the test (Fig. 4.21). Varying retentions can be ascribed to variations in effluent composition.

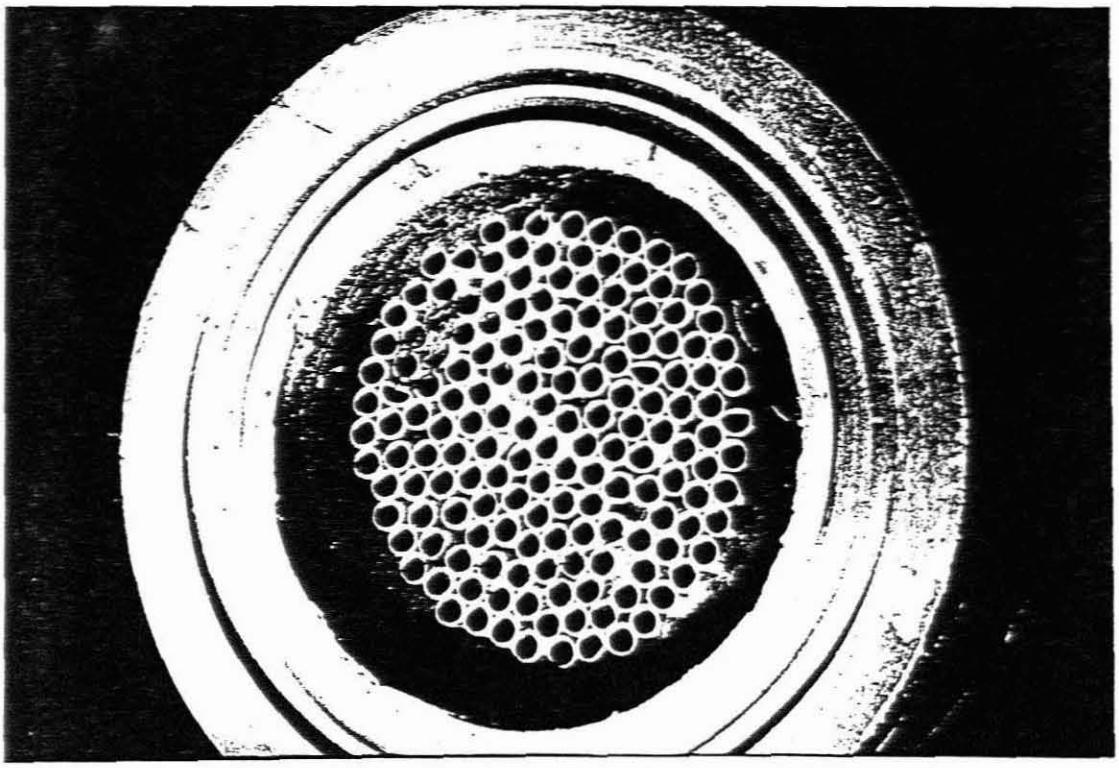


Fig. 4.20:
Bridging at capillary membrane entrance.

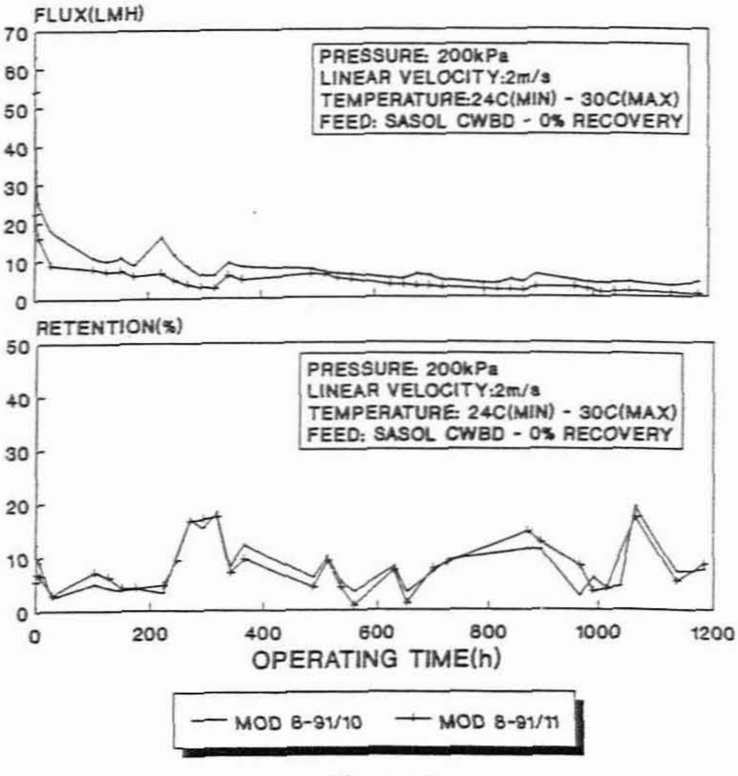


Fig. 4.21:
Flux and retention performances of capillary UF membranes operated on CWBD.

4.7.2.3 *TUBULAR NANOFILTRATION AND RO MEMBRANES*

Nanofiltration membranes

Various experimental PVOH nanofiltration membranes were installed and tested at 2 MPa directly on CWBD effluent (Fig. 4.22). (A conventional CA RO membrane was included as control in the experiment). An advantage of these membranes were that dry storage was posssible, which implied that a system could be shut down for long periods of time without damage to the membranes. Another advantage of the nanofiltration membranes was that higher average fluxes should be obtained when compared to conventional RO membranes so that lower operating pressures would be possible.

Although the general conductivity retention of the PVOH nanofiltration membranes was on average 75% compared with the 99% retention of the CA membranes, analysis of the permeate (Figs. 4.23 - 4.29), showed that the SO_4^{2-} and PO_4^{3-} retentions were comparable to that of the CA membrane (99,9% retention). It was important to remove $CaSO_4$ and phosphates in view of their scale-forming potentials.

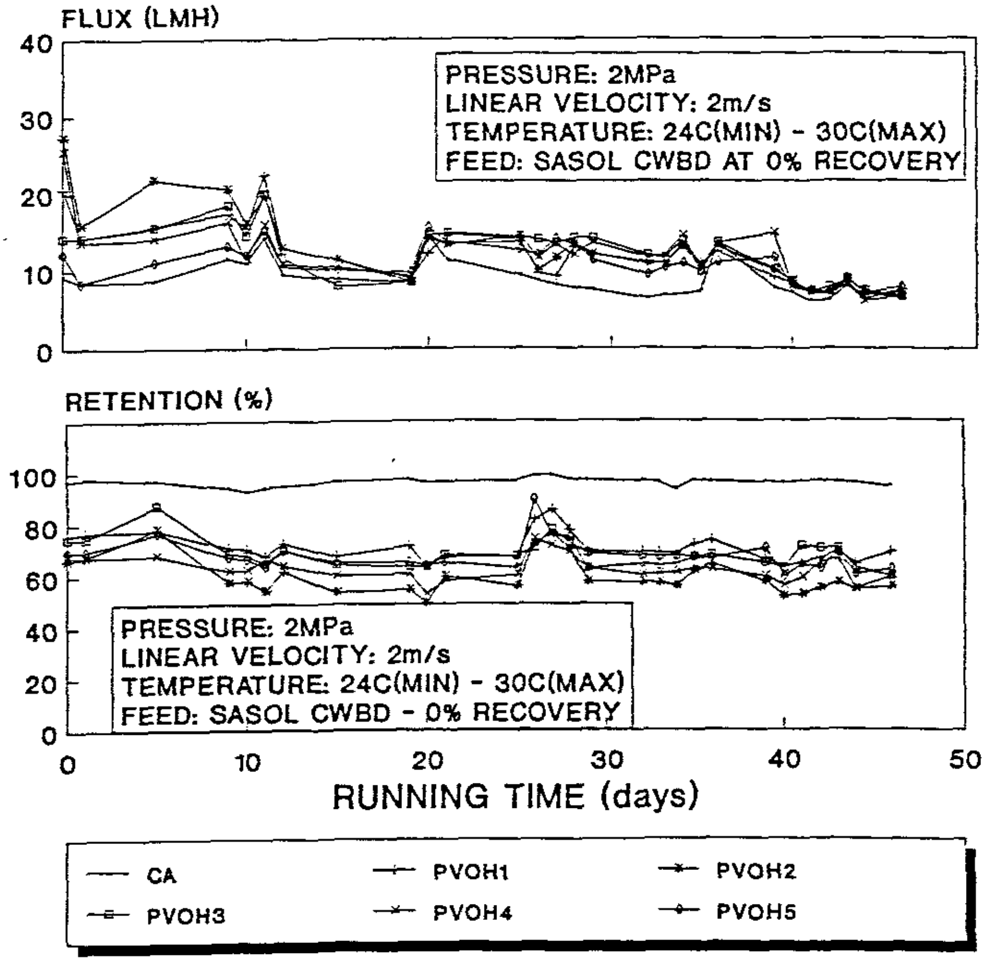


Fig. 4.22:

Flux and retention performances of different NF membranes operated on CWBD.

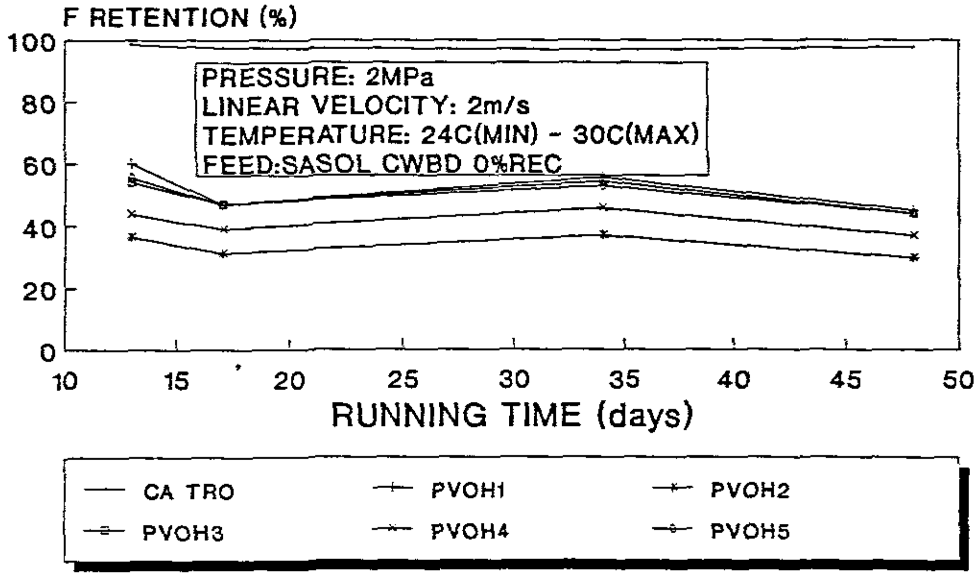


Fig. 4.23:
Fluorine retention - NF membranes.

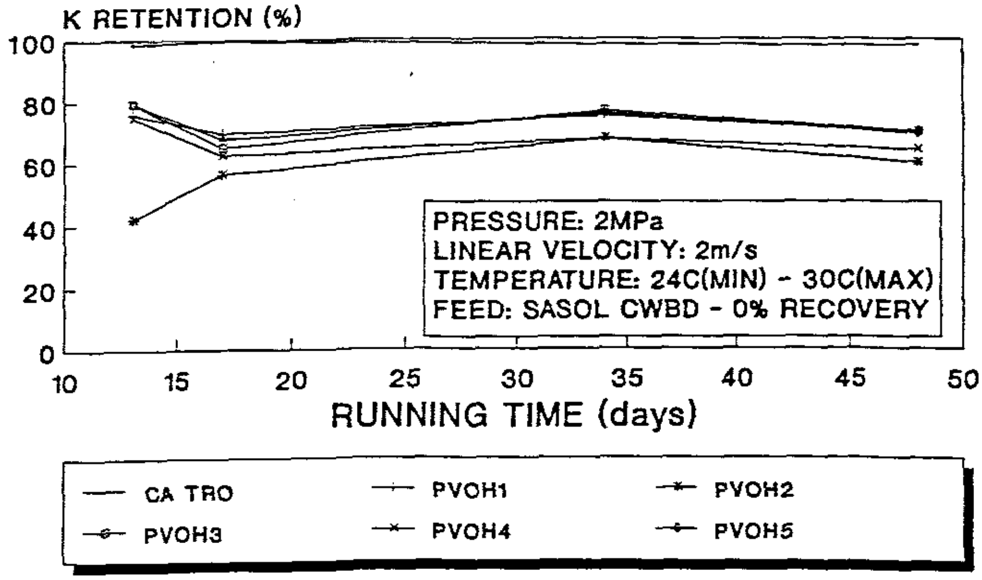


Fig. 4.24:
Potassium retention - NF membranes.

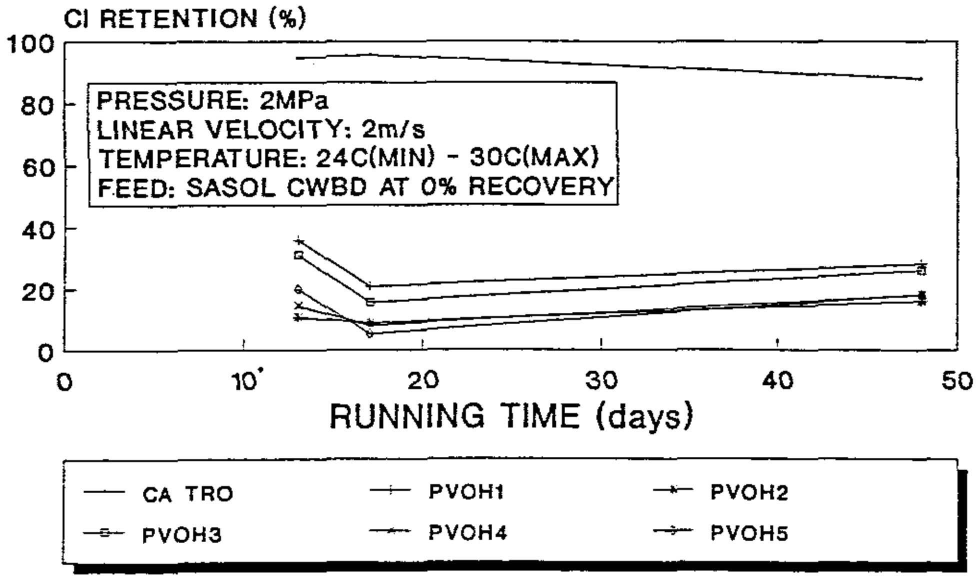


Fig. 4.25:
Chlorine retention - NF membranes.

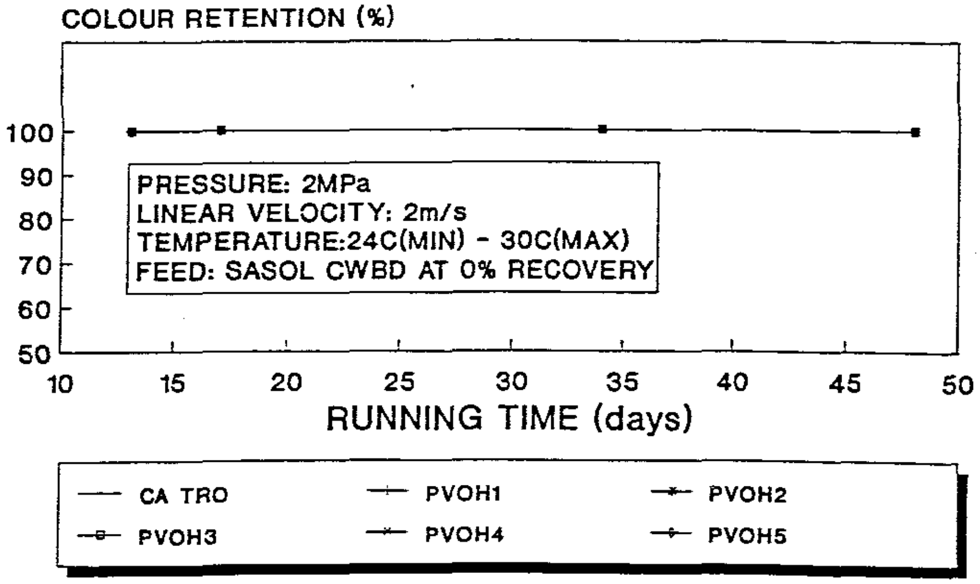


Fig. 4.26:
Colour retention - NF membranes.

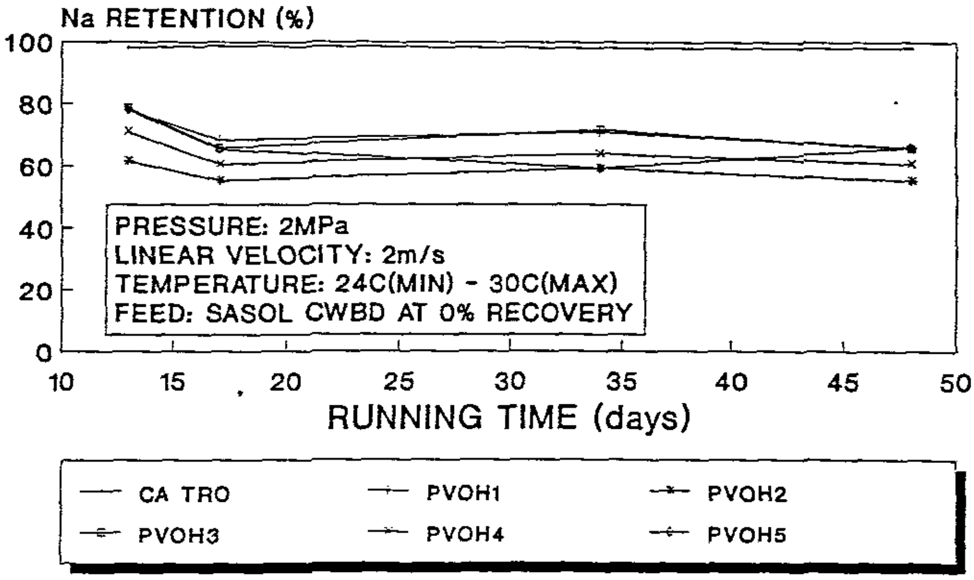


Fig. 4.27:
Sodium retention - NF membranes.

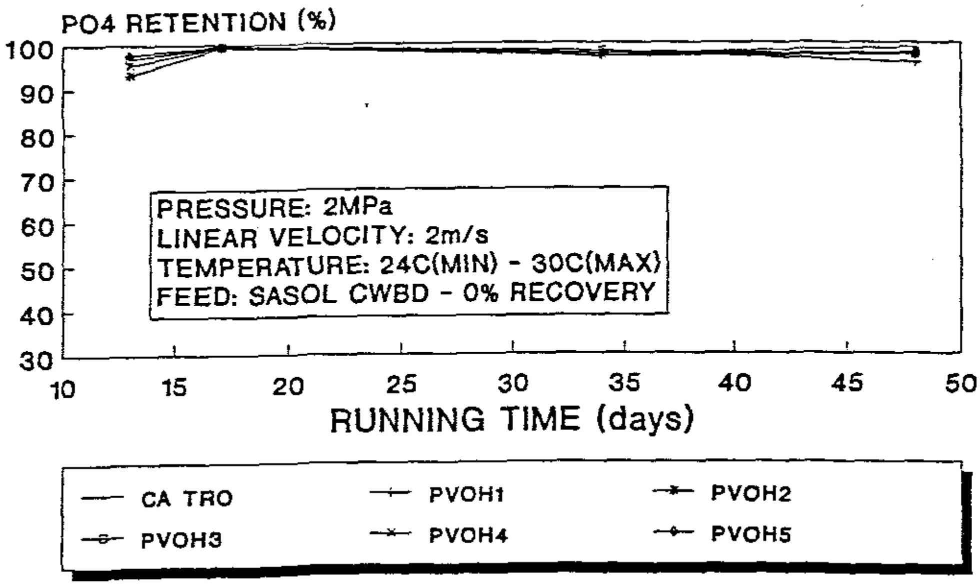


Fig. 4.28:
Phosphate retention - NF membranes.

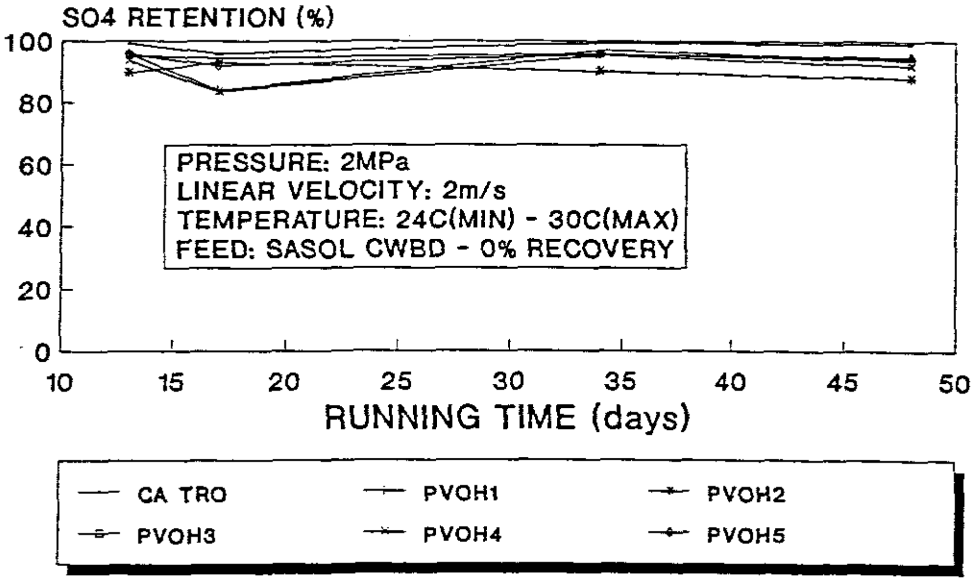


Fig. 4.29:

Sulphate retention - NF membranes.

Modified PVOH RO membranes

Experimental ultra-thin-film modified 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) were tested. When they were tested previously on a 2 000 ppm NaCl solution, retentions of above 94% were obtained with the CAMPIP membrane having a corresponding flux of 60 LMH.

The effluent was again concentrated to give an eventual recovery of 75%. The result was an expected reduction in flux to about 10 LMH with the CAMPIP membrane giving the best results for both flux and retention (Fig. 4.30). The membranes were tested at a relatively low operating pressure of 2 MPa, and higher fluxes can be expected when they are tested at higher pressures.

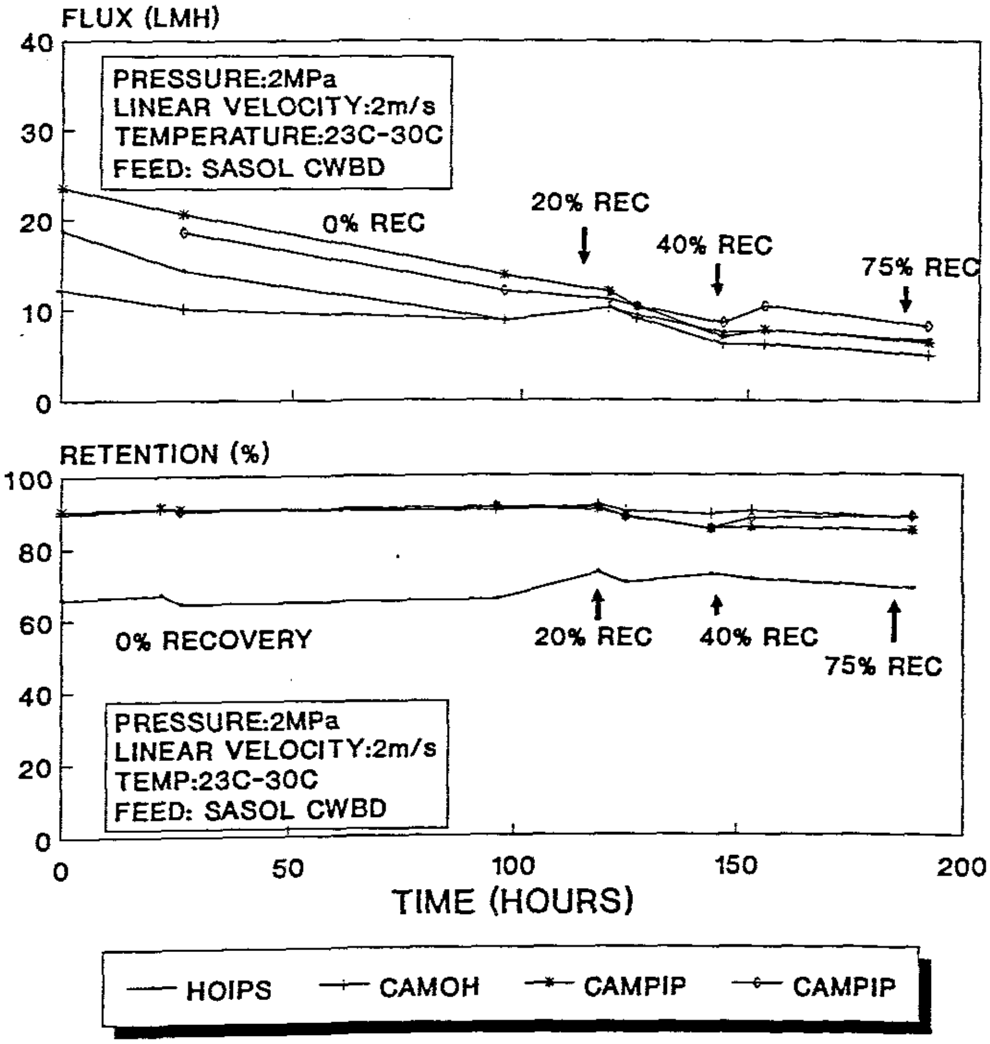


Fig. 4.30:

Flux and retention performances of different PVOH RO membranes operated on CWBD at different recoveries.

4.8. DISCUSSION

UF and RO membranes tested in this study proved, with the exception of a few, to be 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 proved that suspended solids and macromolecules could be effectively removed by UF while the salt concentrations were greatly reduced by RO.

A good quality permeate with 100% suspended solids and close to 100% colour removal was achieved by ultrafiltration. 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 achieve higher average fluxes. It was interesting to note that 50% to 70% of Fe^{3+} and SO_4^{2-} were removed because of a gel-polarized layer on the UF membrane surface. The retention of sulphates should reduce scale formation to a large extent.

In the case of nanofiltration, the biggest problem proved to be the relative rapid, although not permanent, fouling of the membranes. The reason for this can be found by examining the phenomenon of gel-polarization (refer Chapter 6). A general conductivity retention of approximately 70% and a 99% PO_4^{3-}, SO_4^{2-} and colour retention were achieved in the case of NF. Although higher average fluxes were achieved in the case of NF when compared with RO, the flux evened out at more or less the level as RO (after approximately 50 h of operation).

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.

It is safe to say that 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 corresponding average retention of 95%) could be achieved with a RO system operated at 4 MPa. When a mass balance is made over a typical RO unit consisting of a hypothetical number of 660 2,4 m modules (equivalent to 1 000 m^2 membrane area) (Fig. 4.31), the water recovery was found to be 25%. In this case the total maximum CWBD stream of 2 700 m^3/d (equivalent of 112 500 kg/h) was used as feedstream. In practice RO treatment of a smaller sidestream would probably be practical. The power cost incurred could be estimated by calculating the plant productivity [Ref. 4.13] as follows:

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

Where:

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

Power cost incurred = Feed pressure × Feed flow rate

From the above formulas the productivity of a RO plant as stipulated in the mass balance (Fig. 4.31) 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.

In conclusion, it must be accepted that the effluent stream selected for testing of the membranes, namely CWBD, was an extreme case, especially when fouling potential was considered. It is almost certain that membrane performance, especially when membrane flux is considered, will improve when an alternative stream is selected. The opportunity given 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.

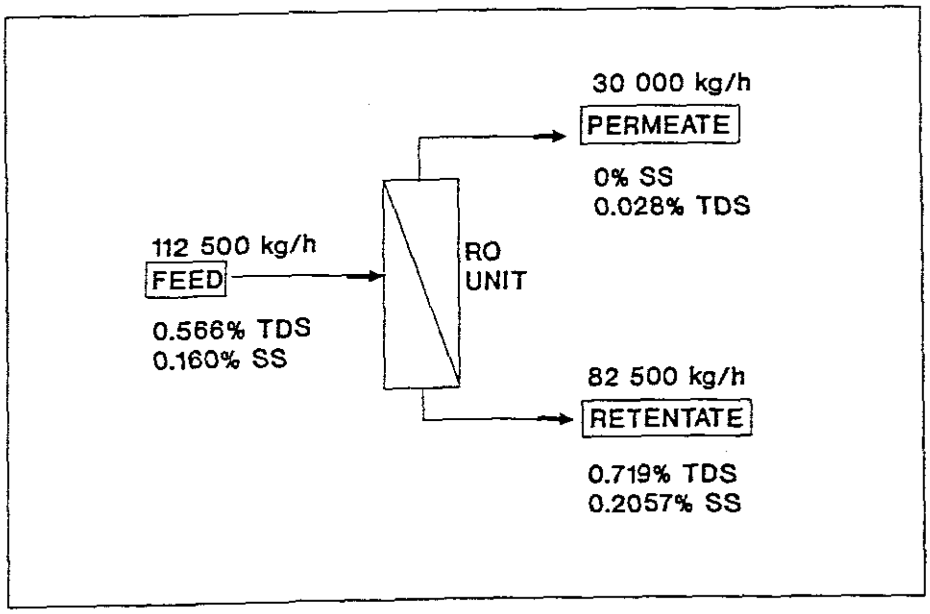


Fig. 4.31:
Mass balance over a typical RO unit.

CHAPTER 5

THE REMOVAL OF POTASSIUM BITARTRATE FROM WINE RESTS WITH PRESSURE-DRIVEN MEMBRANES

5.1 INTRODUCTION

During fermentation and stabilization of wine, wine lees are deposited at the bottom of the stabilization tanks. At present the only 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 cell and protein fractions of wine lees could be valuable by-products as these are sought after products in the food (e.g. yeast extract) and animal feed industry [Ref. 5.1, 5.2, 5.3 and 5.4].

Brennochem, a company which specializes in the extraction of KHT from wine lees, collects the lees from cellars in the Western Cape. For the purpose of this study wine lees was provided by this company for testing on membrane systems.

The study investigated the novel application of membranes to recover potassium bitartrate from wine lees. If applied correctly it may also be possible to recover valuable protein and yeast cells by means of membrane fractionation. To obtain complete separation between high-molecular-mass solutes (proteins and yeast cells) and low-molecular-mass solutes (KHT), the retentate was diluted with a solvent (water) so that the low-molecular-mass solutes were washed out. This type of operation is called diafiltration. Ultrafiltration 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 from the UF was then concentrated by means of RO and nanofiltration to allow subsequent precipitation of the product.

5.2. OBJECTIVE

The main objective of this study was to determine whether membrane processes can be applied successfully to the fractionation of wine lees to produce usable by-products such as yeast cells, cream of tartar and other proteins.

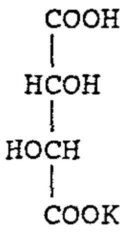
5.3. HISTORICAL BACKGROUND

5.3.1 ORIGIN OF CREAM OF TARTAR

Cream of tartar is also known as potassium bitartrate and potassium acid tartrate (in this study KHT will be used as the abbreviation for potassium bitartrate). 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. 5.1).

$$K^+ + C_4H_5O_6^- \longrightarrow KC_4H_5O_6 \qquad \text{(Eq. 5.1)}$$

$KC_4H_5O_6$ Mol wt:188,18



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

Fig. 5.1:
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 the residues from the wine industry for general-purpose use in industry.

5.3.2 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,
(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 [Ref. 5.5, 5.6 and 5.7],
(ii) the contact process [Ref. 5.5, 5.8 and 5.9].

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 [Ref. 5.10 and 5.11]. A typical system is shown in Figure 5.2.

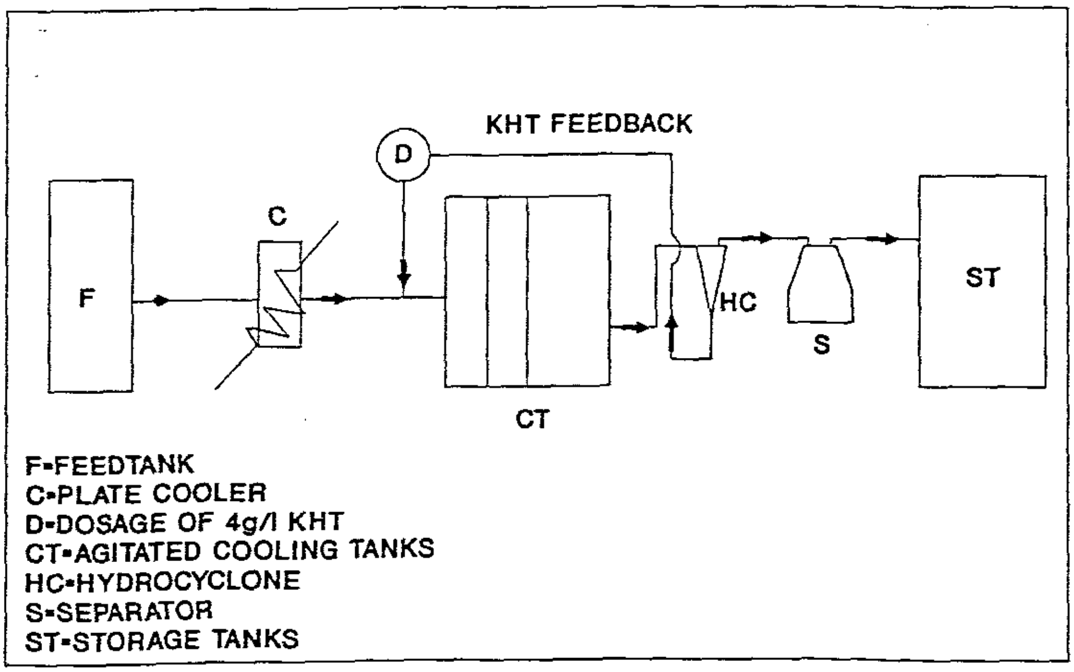


Fig. 5.2:
The Contact Process for KHT stabilization.

5.3.3 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. 5.12]. Wine tartrates have been found to contain 0,011 to 0,064% protein fraction.

The yeast cell and protein fraction of wine is often present as colloidal or macromolecular structures. It is this component of wine, together with impurities, that inhibits tartrate crystallization. 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. 5.13]. 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. 5.14] 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 1 000 000 dalton and 10 000 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 of less than 10 000 dalton.

A large portion of wine lees consists of proteins and yeast cells [Ref. 5.15]. These constituents of wine lees is bound to cause problems in the fractionation of the lees because of the KHT affinity for proteins and yeast cells.

The methods used for KHT extraction from wine lees usually include the use of different chemical methods [Ref. 5.16]. 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. 5.17].

5.4. WHY MEMBRANE SYSTEMS?

The above outline indicates the complexity of fractionating wine lees. First of all, it must be realized that at present the most important by-product of wine lees is potassium bitartrate. Another possible valuable by-product would be the protein-rich yeast cells.

The colloids and macromolecules in wine lees could possibly be separated by ultrafiltration, and reverse osmosis could be used to retain KHT. A number of problems can be foreseen:

(i) certain proteins can foul membranes rapidly;
(ii) previous experimental data show that a certain fraction of the KHT has an affinity for certain proteins and colloids, so that it would therefore be difficult to remove all of the KHT present in the wine lees.

Brennochem buys the wine lees as a by-product from wine cellars, therefore before processing can begin the wine lees are transported over large distances to the factory. 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 is used to recover the potassium bitartrate (Fig. 5.3). 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, 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;

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

5.5 THE CHEMICAL PROCESS

The hydrocyclone/calcium process (see Fig. 5.3) consists mainly of chemical separation methods and a combination of physical separation methods, which includes the use of hydrocyclones and centrifuges.

The feed which consists of approximately 6% solids is first fed to a series of hydrocyclones where it is split into two streams. The main purpose of the hydrocyclones is to separate the KHT crystals from the wine solids and yeast cells. The temperature is then increased to 50 °C to dissolve most of the KHT. $CaCO_3$ is then fed to the KHT solution and CaT and K_2T are formed (Eq. 5.2). The CaT is insoluble in water and precipitates immediately, while the K_2T remains in solution. These two substances are then separated by means of a vacuum filter.

The cake fraction contains a small amount of K_2T and a relatively large percentage of CaT. When sulphuric acid is added to CaT, H_2T is formed (Eq. 5.5). The small amount of K_2T reacts with a certain amount of the H_2T and forms KHT (Eq. 5.4). This slurry is then transferred to a filter press where the yeast is separated from the H_2T and KHT solutions.

The filtrate from the vacuum filter consists mainly of water and dissolved K_2T. At this point KHT and H_2T collected from the filter press are added to the stream together with additional KOH (Eq. 5.3 and 5.4). The product, KHT crystals, is formed and separated in the last step by centrifuge. The water is added to the feed stream as make-up.

Chemical reactions involved in the calcium process are:

$$2KHT + CaCO_3 \longrightarrow CaT\downarrow + K_2T + CO_2 + H_2O \qquad \text{(Eq. 5.2)}$$

$$KHT + KOH \longrightarrow K_2T + H_2O \qquad \text{(Eq. 5.3)}$$

$$K_2T + H_2T \longrightarrow 2KHT \qquad \text{(Eq. 5.4)}$$

$$CaT + H_2SO_4 \longrightarrow CaSO_4 + H_2T \qquad \text{(Eq. 5.5)}$$

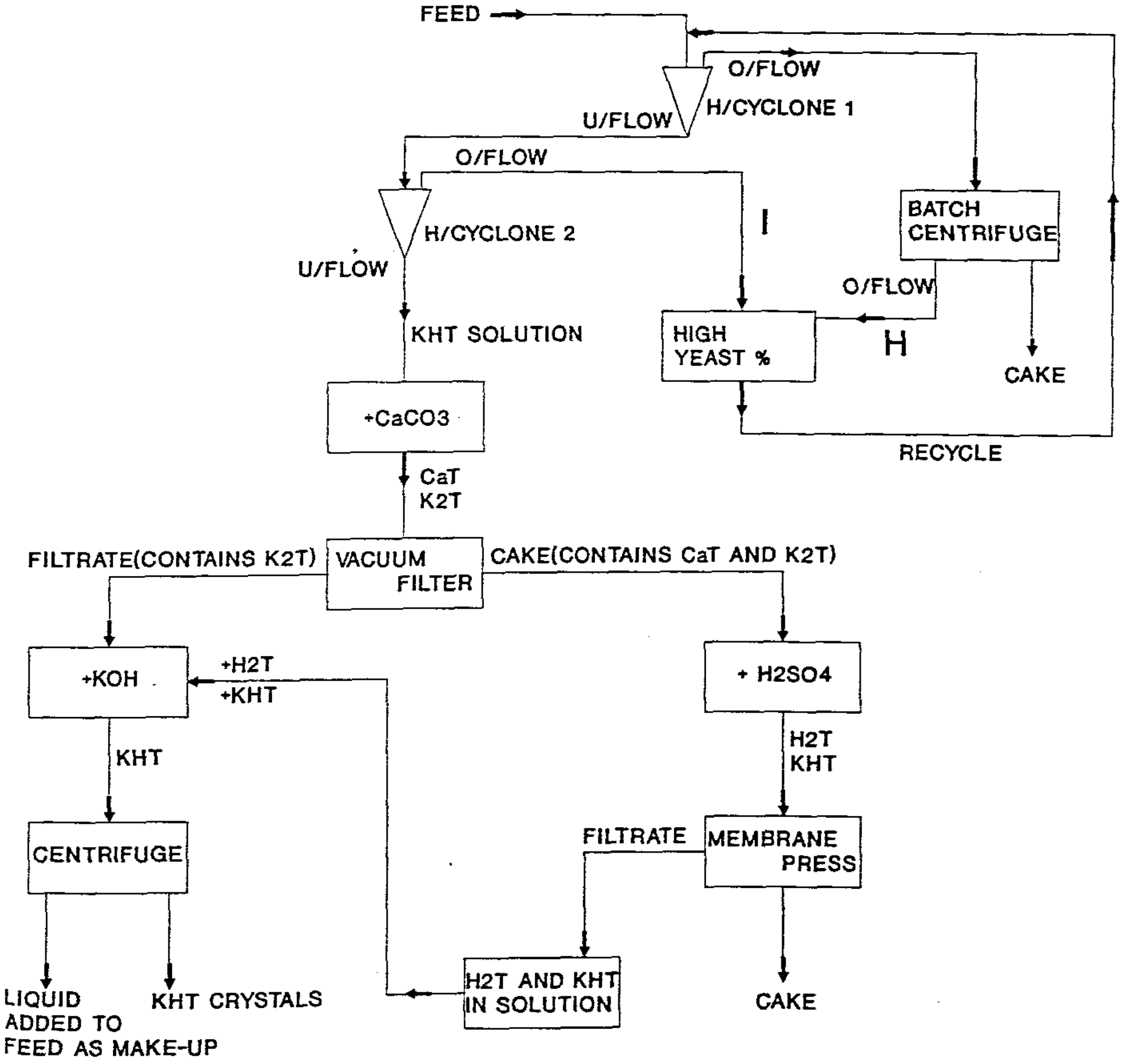


Fig. 5.3:

Schematic presentation of the Hydrocyclone/Calcium process.

5.6. MEMBRANE PROCESSES AS ALTERNATIVES TO THE EXISTING CHEMICAL PROCESS

5.6.1 PROBLEMS THAT MAY ARISE

Various membrane separation systems have to be tested before a decision on any possible method can be made. Problems that may arise and questions that must be asked when deciding on possible membrane systems are:

(i) Will fouling of membranes occur, resulting in uneconomic fluxes - especially in the case of UF membranes;
(ii) Is there the possibility of a larger 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 used in RO;
(v) Will traditional RO membranes be resistant to KHT crystal formation and how would this influence their flux;
(vi) Will it be possible to replace the existing system with a more compact and effective system ?

5.6.2 MEMBRANE SYSTEM COMBINATIONS

5.6.2.1 *COMBINED UF AND RO SYSTEM*

As shown in Fig. 5.4, the system consists of a UF and an RO unit. The wine-lees cake is mixed with water and concentrated by ultrafiltration. 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. 5.5), 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 as efficient as far as flux and operating pressures are concerned. In this regard it is fortunate that KHT has poor solubility and therefore the osmotic pressure would be low, and consequently a low operating pressure is necessary.

It is also possible that a nanofiltration membrane rather than an RO membrane could be used, because KHT is a relatively large molecule with a molecular mass of 188,8. Operating pressures would be lower when a nanofiltration membrane is used rather than an RO membrane. An experimental PVOH nanofiltration membrane is available and could be used.

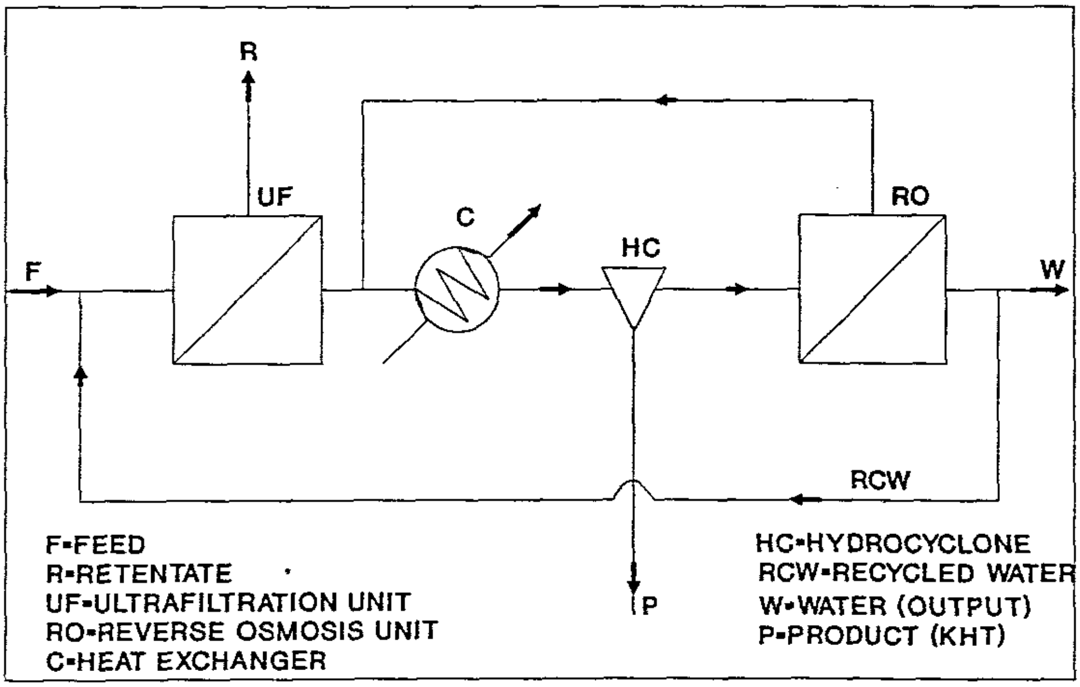


Fig. 5.4:
KHT recovery - combined UF and RO system.

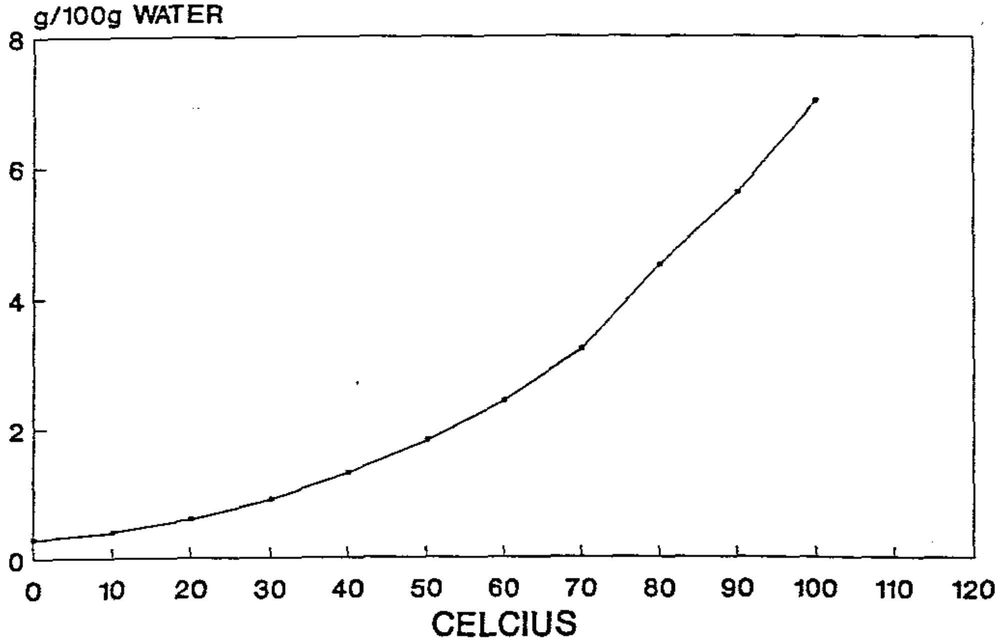


Fig. 5.5:
Solubility curve of KHT in water.

5.6.2.2 *COMBINATION OF UF AND CHEMICAL TREATMENT*

Another system that could be used is a combination of ultrafiltration and chemical treatment (see Fig. 5.6). Basically, the slurry would be treated with UF to separate the yeast cells and proteins from the KHT-rich solution. The UF permeate could then be chemically treated to form 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 chemical reactions are:

$$2KHT + Ca(OH)_2 \longrightarrow CaT\downarrow + K_2T + 2H_2O \qquad \text{(Eq. 5.6)}$$

$$CaT + H_2SO_4 \longrightarrow CaSO_4 + H_2T \qquad \text{(Eq. 5.7)}$$

$$K_2T + H_2T \longrightarrow 2KHT \qquad \text{(Eq. 5.8)}$$

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.

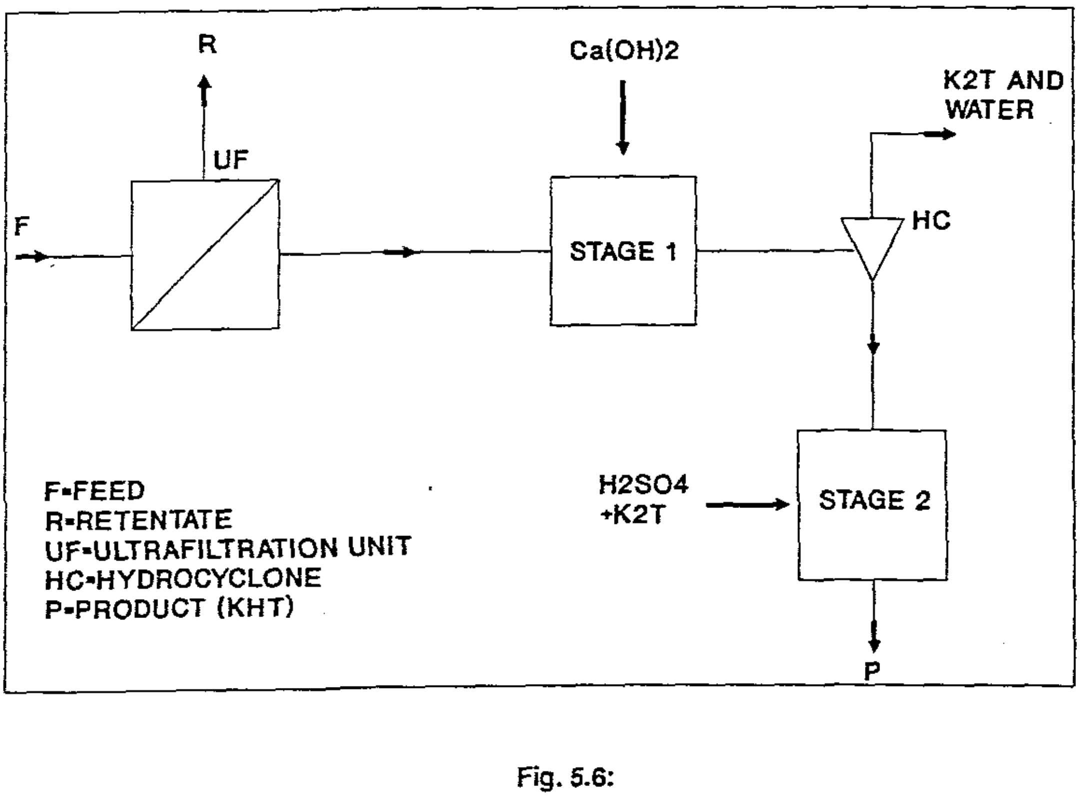


Fig. 5.6:
KHT recovery - UF and chemical process combination.

5.6.2.3 *OTHER COMBINATIONS*

Combinations of the above two systems can be used in conjunction with the existing chemical process. At present, streams I and H (Fig. 5.1) in the chemical process are recycled but this process is inefficient. Use of a membrane separating system as indicated in the above two methods could improve efficiency.

5.7 EXPERIMENTAL

5.7.1 OBJECTIVES

The objectives were to:

(i) determine the number of cycles in which the slurry had to be washed 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 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.

5.7.2 PLANNING OF EXPERIMENTS

5.7.2.1 *UF MEMBRANE TESTING*

A range of UF membranes were tested on single-cell test-rigs designed for the purpose. 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 it to a fine suspension.

In order to calculate the concentrations of solids accurately, 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.

5.7.2.2 *RO MEMBRANE TESTING*

Permeate collected from UF membranes was used to test RO and nanofiltration membranes. The KHT solution was concentrated to a point at which precipitation would take place readily. 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 nanofiltration membranes (PVOH and CA) were tested on the KHT solution. It was possible that the nanofiltration membranes would give higher fluxes than the CA membranes with more or less the same retention, since KHT has a relatively high molecular mass (188 g/mol).

5.7.2.3 *KHT CONCENTRATION DETERMINATION*

A method of determining KHT concentration had to be found as it was important to know the concentration KHT present in the feed and permeate streams. Titration with NaOH was found to be the easiest and quickest method. The method is not entirely accurate because all acids present in the sample are determined as tartaric acid. The error is, however, negligible.

Reaction

$$\mathrm{KHT} + \mathrm{NaOH} \longrightarrow \mathrm{K^+} + \mathrm{T^{2-}} + \mathrm{Na^+} + \mathrm{H_2O} \qquad \text{(Eq. 5.9)}$$

Apparatus needed

100 ml Erlenmeyer, burette.

Solution needed

0,1 N NaOH solution.

Test procedure - Titration

Titration A

Take 2 ml sample from feedtank and add 25 ml water.

Heat and stir.

Add 0,5 ml flocculant.

Add 1 - 3 drops phenolphthalein.

Titrate with 0,1 N NaOH solution.

Titration B

Take permeate from UF membranes and titrate as above (no flocculant added).

Calculation of KHT concentration

$$C_1V_1 = C_2V_2$$

$$C_1V_1/C_2V_2 = 1/1$$

$$\therefore \quad C_1 = C_2V_2/V_1 \qquad \text{(Eq. 5.10)}$$

Where:

C_1V_1 = KHT solution

C_2V_2 = NaOH solution

V_2 = volume titrated NaOH

C_2 = conc. NaOH (= 0,1 mol/dm^3) (= 4 g/ℓ)

V_2 = KHT sol. volume (0,002 dm^3).

C_1 = conc. KHT solution (unknown)

mol. mass of KHT = 188,18

From (Eq. 5.10):

$$C_1 = (0{,}1 \times V_2/0{,}002) \text{ mol/dm}^3$$

$$= \{(0{,}1 \times V_2/0{,}002) \times 188{,}18\} \text{ g/dm}^3$$

$$= (9409 \times V_2) \text{ g/dm}^3$$

$$= (940{,}9 \times V_2) \text{ g/100 m}\ell$$

$$\text{Put } X = (V_2/1000) \text{ m}\ell$$

$$\therefore \; C_1 = (0{,}941 \times X) \text{ g/100 m}\ell$$

Where:

X = mol NaOH titrated in mℓ

∴ C_1 = % KHT present in solution C_1

True percentage KHT would be = $\{C_1/(100+C_1)\} \times 100$

KHT(A) − KHT(B) = KHT adsorbed to suspended solids and proteins if no undissolved crystals are present in the sample.

5.8 TEST RESULTS

5.8.1 UF MEMBRANE TEST RESULTS

The purpose of 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 were tested on wine lees containing various solids concentrations, namely 1,7%, 2,6%, 5% and 10% (see Figures 5.7 to 5.10). Although difficulties were encountered with equipment during testing on high solids concentrations, no visible damage was done to the membrane surface. Permeate fluxes became 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. During the first three tests (Fig. 5.7 - 5.9), UF membranes with different MMCOs were tested.

The MMCOs of the membranes tested on PEG were:

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

Although there was a difference in quality of the permeate produced by the different membranes, the flux tended to stabilize at approximately the same value of 50 LMH. It was therefore decided to use a standard commercial membrane for further testing (719). 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. 5.11). From the data it was clear that a certain percentage of the KHT was retained. This was either caused by a gel layer on the membrane surface or the affinity between KHT and the yeast cells. Fig. 5.11 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. 5.10 and 5.12). 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 drop in permeate flux. Permeate from this experiment was collected for further trial tests on nanofiltration 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.

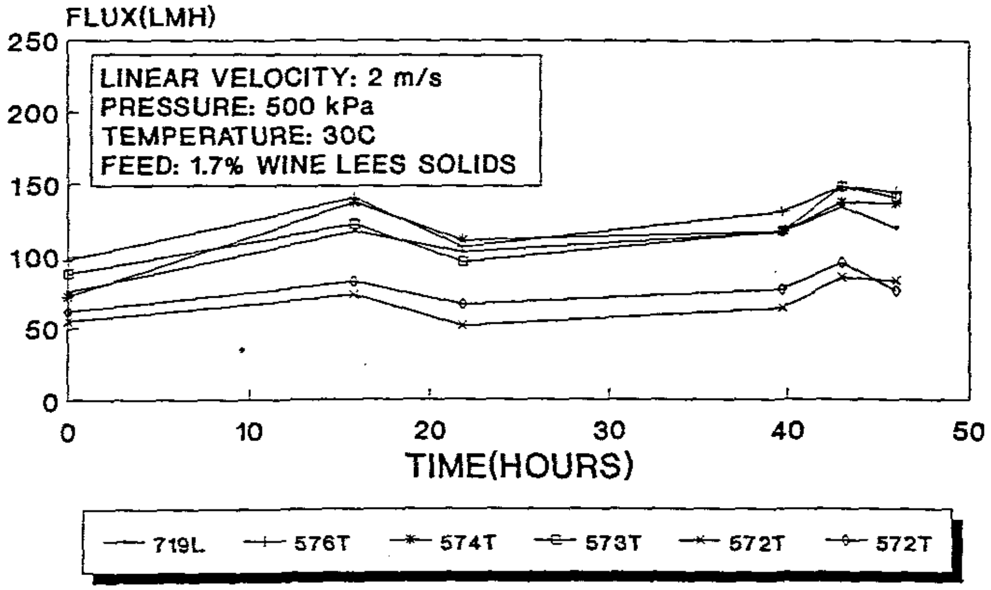


Fig. 5.7:
Flux performance of different UF membranes operated on a 1,7% wine lees solids slurry.

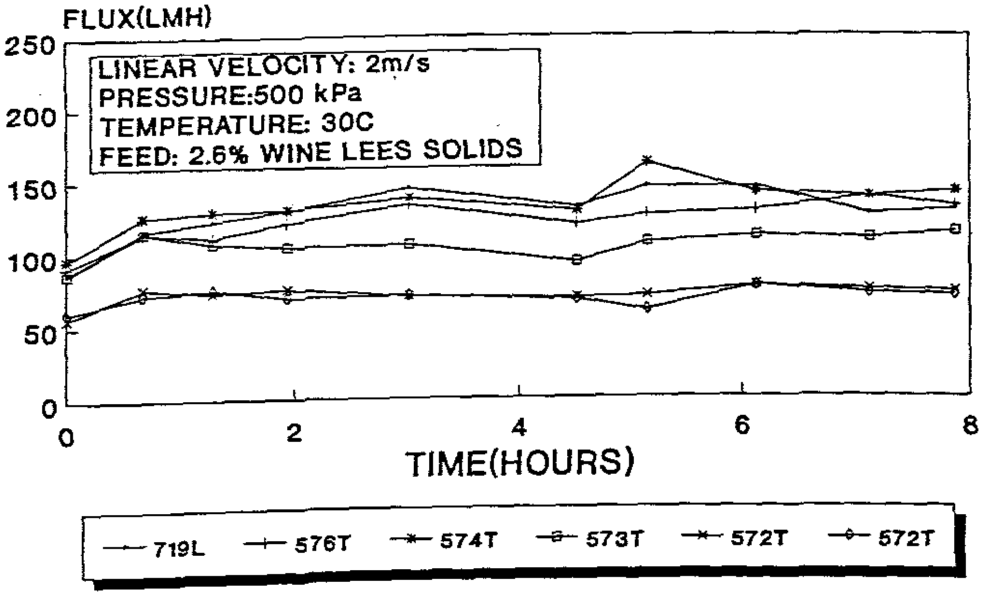


Fig. 5.8:
Flux performance of different UF membranes operated on a 2,6% wine lees solids slurry.

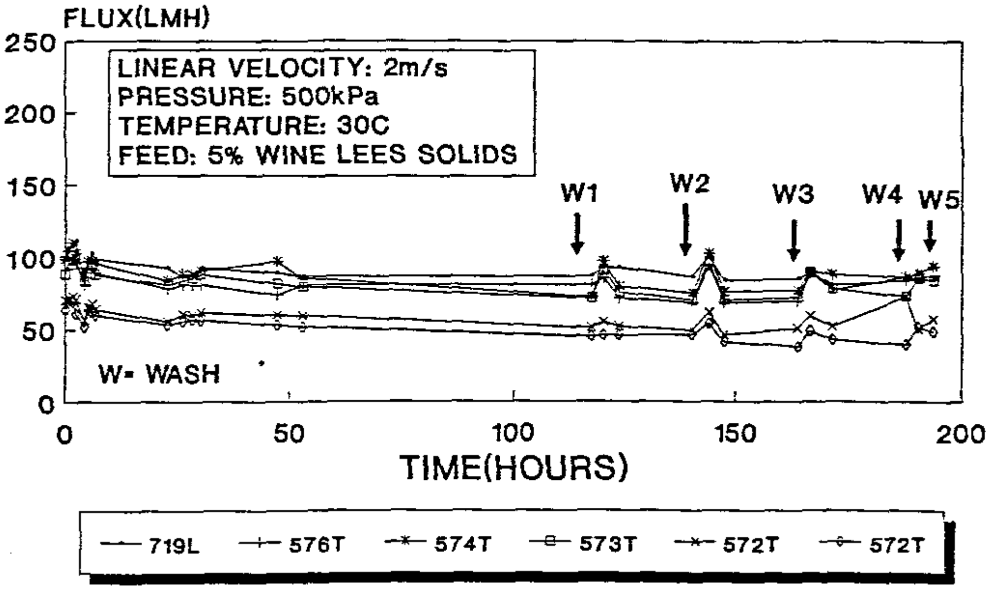


Fig. 5.9:
Flux performance of different UF membranes operated on a 5% wine lees solids slurry.

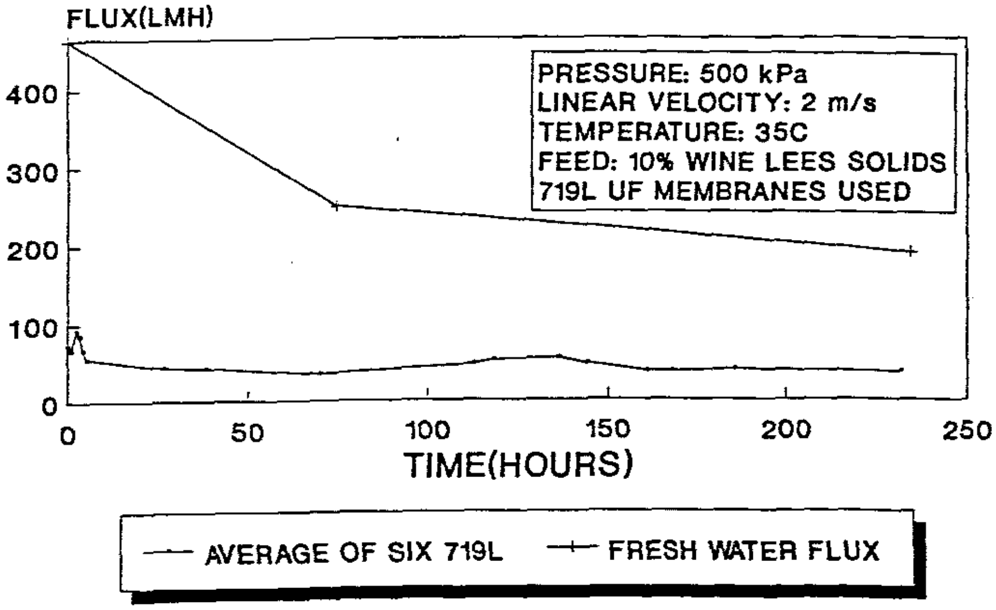


Fig. 5.10:
Flux performance of UF membranes operated on a 10% wine lees solids slurry.

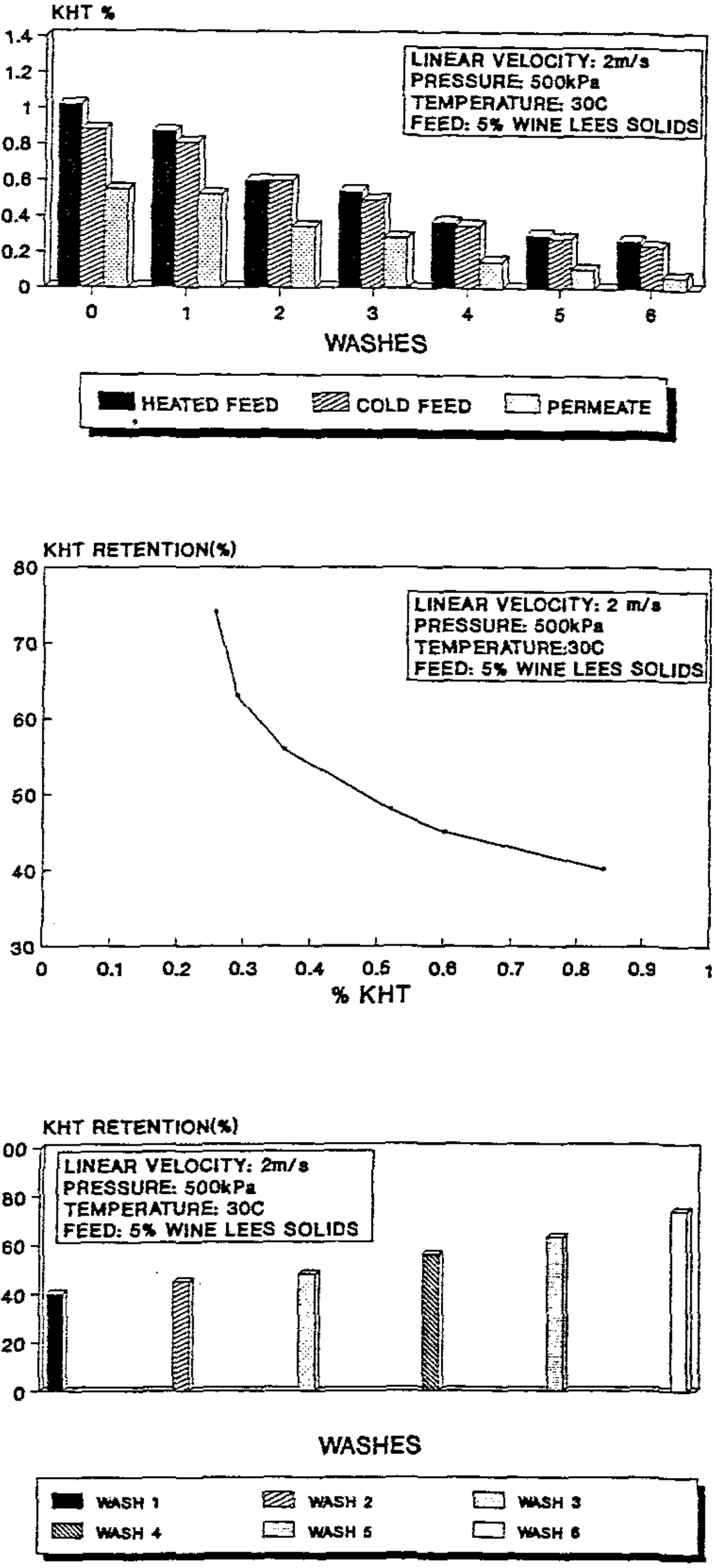


Fig. 5.11:

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

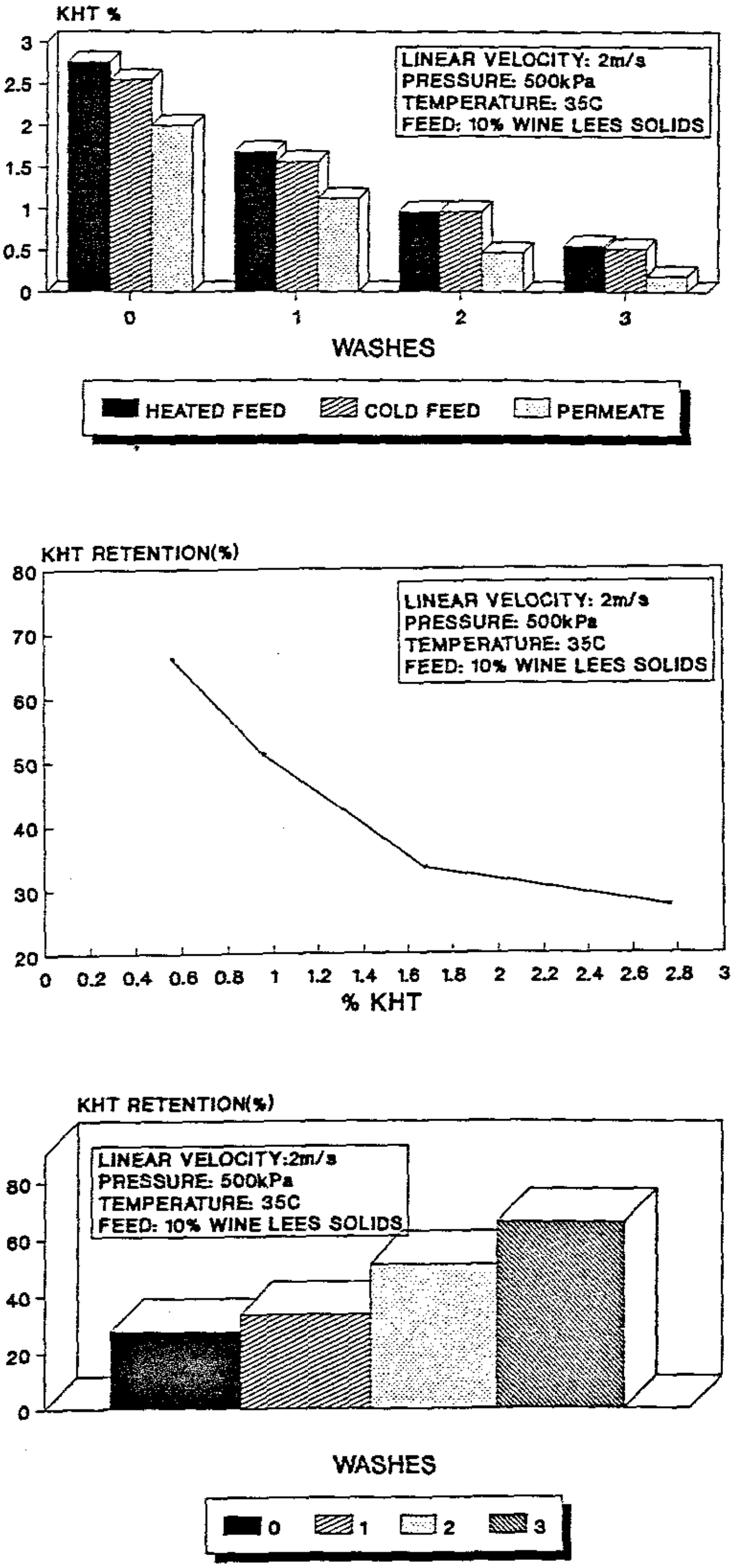


Fig. 5.12:

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

5.8.2 RO MEMBRANE TEST RESULTS

Permeate collected from the 10% wine lees solids was used to test different RO and nanofiltration membranes (Fig. 5.13 and 5.14). When the UF permeate was concentrated to 85%, precipitation of KHT crystals was rapid.

Figure 5.14 shows a decline in flux with increasing recovery when CA RO membranes were tested on the UF permeate. This was unexpected because the KHT precipitation should have maintained the real concentration at a constant level. However, the UF membranes still allowed smaller proteins to go through and, because of this, concentration of these proteins occurred when RO or NF were applied, and as a result a reduction in permeate flux occurred. 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 ultrafiltration membrane and subsequently reduce the amount of smaller proteins in the permeate, or even eliminate them. However, decreasing the MMCO of the UF membrane could result in an increase in KHT retention.

The PVOH nanofiltration membrane had a pure-water flux more than double that of the CA RO membrane, and therefore higher fluxes for the nanofiltration membrane were expected during operations on the KHT solution. However, after the operation was started, the flux immediately decreased to unacceptable levels, and the membranes were therefore removed. An experimental nanofiltration 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.

Figure 5.13 shows a dramatic reduction in flux of the experimental CA nanofiltration 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. Compaction is the mechanical deformation of a polymeric membrane matrix which occurs in pressure-driven membrane operations. At elevated pressures, the membrane structure densifies, and the result is a permanent decline in flux. Lower operating pressures for NF membranes should thus result in a higher constant permeate flux.

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.

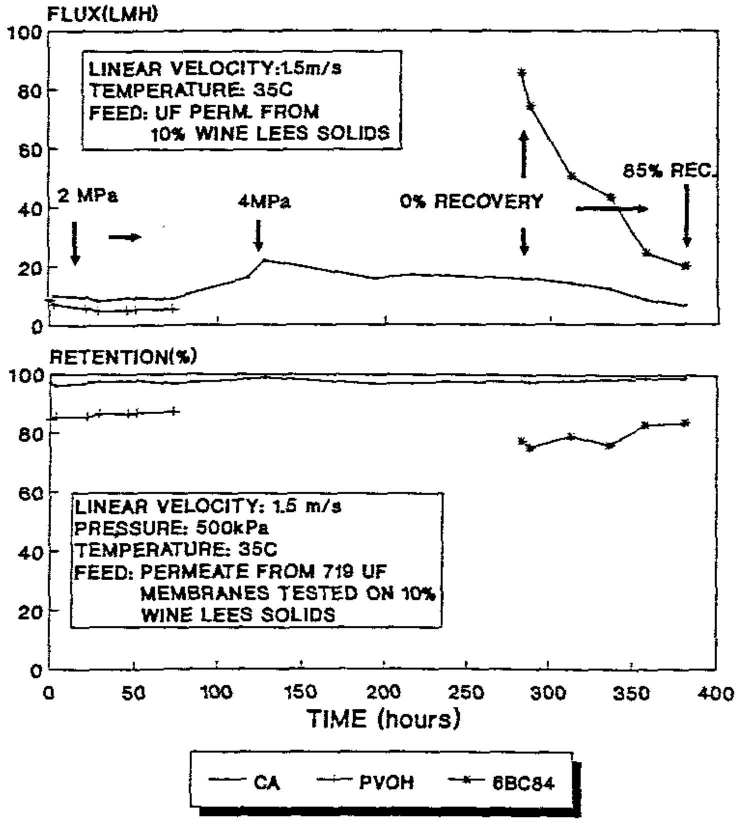


Fig. 5.13:
Flux and retention performances of RO and NF membranes operated on permeate collected from UF.

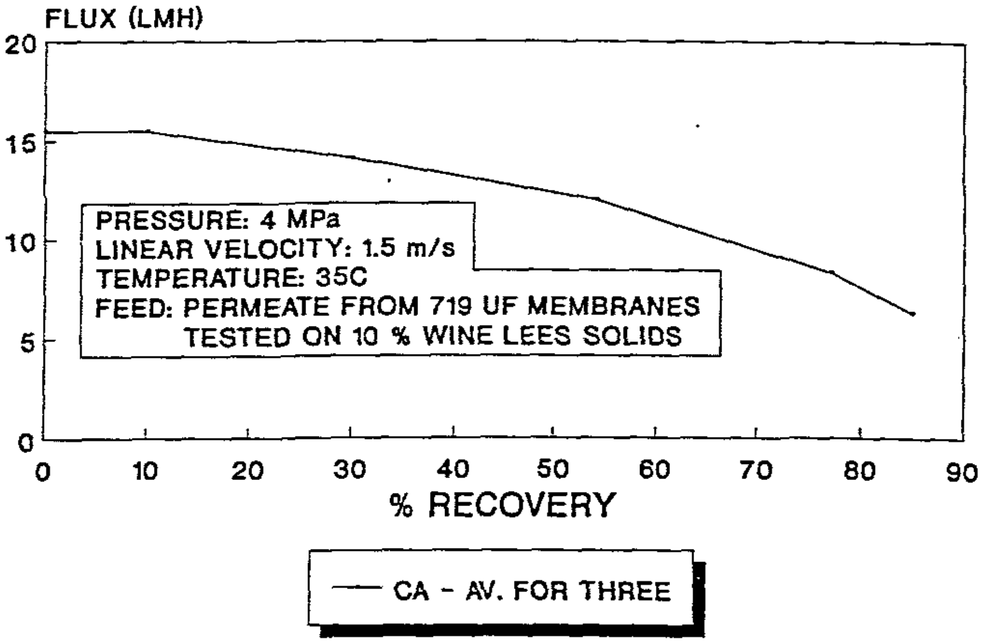


Fig. 5.14:
Performance of reverse osmosis membranes (CA) operated on permeate collected from UF.

5.9 UF/NF COMBINATION AS A SEPARATION SYSTEM

5.9.1 UF/NF SYSTEM

This system has been described in broad terms earlier in the text (refer Section 5.6.2 and Fig. 5.4). Research showed that nanofiltration would probably be more effective than RO because of higher average fluxes obtained by NF. For this reason it was decided to incorporate an NF unit rather than an RO unit in the system.

The proposed system (Fig. 5.18) consists of a mixing unit (Fig. 5.15), UF unit (Fig. 5.16), storage tanks, an in-line centrifuge and a nanofiltration unit (Fig. 5.17). An additional item would probably be a high-shear-rate blender to ensure formation of a homogeneous suspension before entering the UF unit.

All calculations were done on the basis of 1 ton of wine lees to be processed per day. It was also assumed that the lees contained an average of 50% moisture.

Through calculation it was determined that 1 250 ℓ/h water is needed to dilute the wine lees to a 5% solids slurry. However, stream K (Fig. 5.18) could contribute 674 ℓ/h of high-quality water. This sidestream has the added advantage that it contains 0,3% KHT and would therefore increase the efficiency of the UF diafiltration unit.

Calculation showed that 7,5 kg per hour KHT will go to waste if there was no further dilution of the UF system. To avoid this, stream P could be diluted with water as was done in tests, and subsequently diafiltered until most of the KHT was separated from the yeast cells and protein fraction. It is important to note that all the KHT present in the slurry is not necessarily in solution and that more than one "wash" might be required to remove most of the KHT.

Also, in practice, a slight retention of KHT will occur at the UF membrane surface because of:

(i) gel polarization,
(ii) the protein and yeast cell affinity for KHT.

Previous tests have shown that the effects of gel polarization are greater when the ratio of yeast cells to KHT in solution are high. The amount of washes will thus depend on the amount of KHT present in the slurry. The higher the KHT fraction, the more effective will ultrafiltration be.

The best way to operate the nanofiltration unit would be on a batch basis. One must remember that the KHT solution entering the NF system does contain other contaminating salts and ions. For this reason it would not be wise to keep on concentrating without bleeding in order to discard the saline solution while a fresh batch enters the system. At a 70% water recovery rate at A, it was calculated that 275 ℓ/h would need to be discharged at B. The NF system could, however, be operated at a higher recovery rate, in which case the precipitation rate of KHT crystals would increase. The water discharged at A could be used as make-up water for mixing.

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.

5.9.2 CALCULATION OF MASS BALANCES OVER UF/NF SYSTEM

5.9.2.1 *MASS BALANCE OVER MIXING UNIT (FIG. 5.15)*

Assumptions:

- 1 ton wine lees per day = 125 kg/h;
- wine lees contains 50% moisture on average;
- a 95% water content after mixing (5% solids).

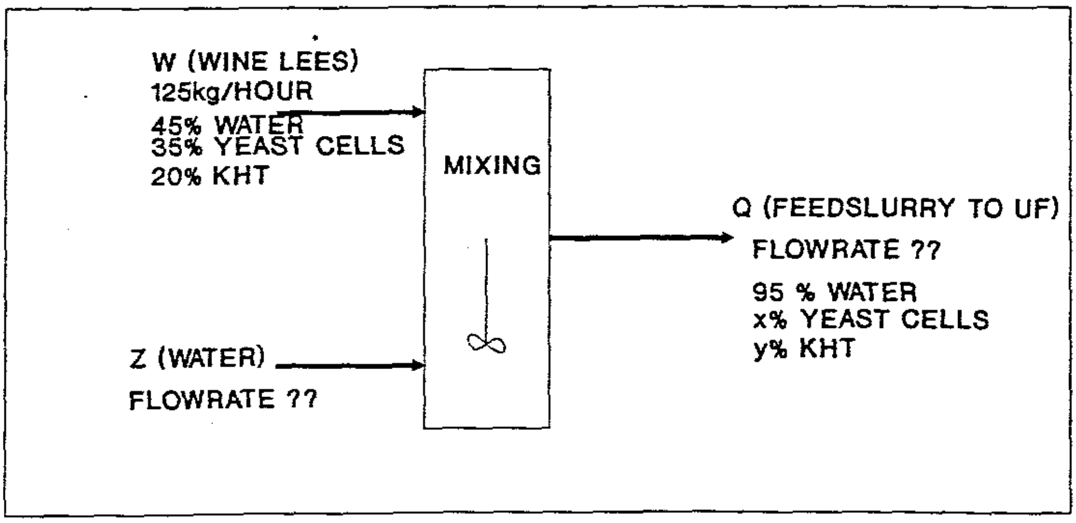


Fig. 5.15:
Mixing unit.

Total balance:

$$W + Z = Q \quad \Rightarrow \quad Z = Q - 125 \qquad \text{(Eq. 5.11)}$$

and

$$0{,}45(W) + Z = 0{,}95(Q) \qquad \text{(Water balance)}$$

From Eq. 5.11

$$0{,}45(125) + (Q - 125) = 0{,}95(Q)$$

$$\therefore Q = 1375 \text{ kg/h}$$
$$Z = 1250 \text{ kg/h}$$

To calculate x and y:

$$0{,}35(W) + Z(0) = x(Q) \qquad \text{(Yeast cell balance)}$$

$$\therefore 0{,}35(125) + 0 = x(1375)$$

$$\therefore x = 3{,}18\% \text{ (yeast cell fraction)}$$

$$y = 1{,}82\% \text{ (KHT fraction)}$$

5.9.2.2 *MASS BALANCE OVER UF UNIT (FIG. 5.16)*

Assumptions:

- average flux through UF membranes = 50 LMH (See Fig. 5.11 and 5.12);
- the effect of gel polarization is not accounted for (assuming the UF membranes retain no KHT);
- membrane module length of 2,4 m with effective membrane length of 2 m;
- 70% water/KHT solution recovery.

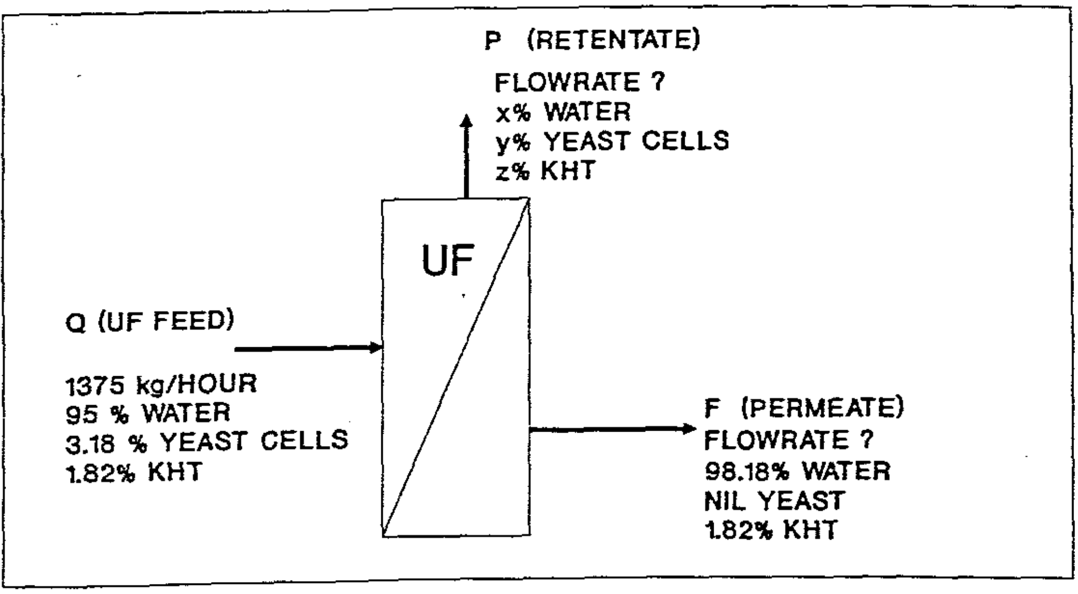


Fig. 5.16:
Ultrafiltration unit.

Calculations:

For a 70% water/KHT solution recovery:

$$F = 0{,}7(Q) = 0{,}7(1375) = 963 \text{ kg/h}$$
$$P = 412 \text{ kg/h}$$

The number of modules needed for the above:

$$\text{Membrane area} = (\pi \times d \times l) \times N$$

Where:

d = inside diameter of tubular UF membranes.
l = effective membrane length
N = number of tubes/module

$$\text{Membrane area} = (\pi \times 0{,}0127 \times 2) \times 19$$
$$= 1{,}52 \text{ m}^2$$

$$\text{Flux/module} = (50 \text{ LMH} \times 1{,}52) = 76 \text{ ℓ/h}$$

$\therefore$ number of 2,4 m modules required = $F/76 = 963/76$ = about 13 modules

The KHT concentration in the permeate (F) will be the same as in the UF feed (Q), when assuming that no retention takes place at the UF membrane surface.

Calculation of the yeast cell fraction in retentate (P):

$$0{,}0318(Q) = y(P) = y(412)$$
$\therefore \quad y = 10{,}6\%$ (after 1 h of operation)

Calculation of KHT% in P:

$$0{,}0182(Q) = z(P) + 0{,}0182(F)$$
$$\therefore 0{,}0182(1375) = z(412) + 0{,}0182(962)$$
$$\therefore z = 1{,}82\% \text{ KHT}$$

This is equivalent to 7,5 kg/h KHT that is lost if there is no further dilution with clean water.

5.9.2.3 *MASS BALANCE OVER NF UNIT (FIG. 5.17)*

Assumptions

- average flux of 25 LMH through nanofiltration membranes (See Fig. 5.13);
- a 70% water recovery;
- a 2,4 m module length, with a 2 m effective membrane length;
- an operating temperature of 40 °C.

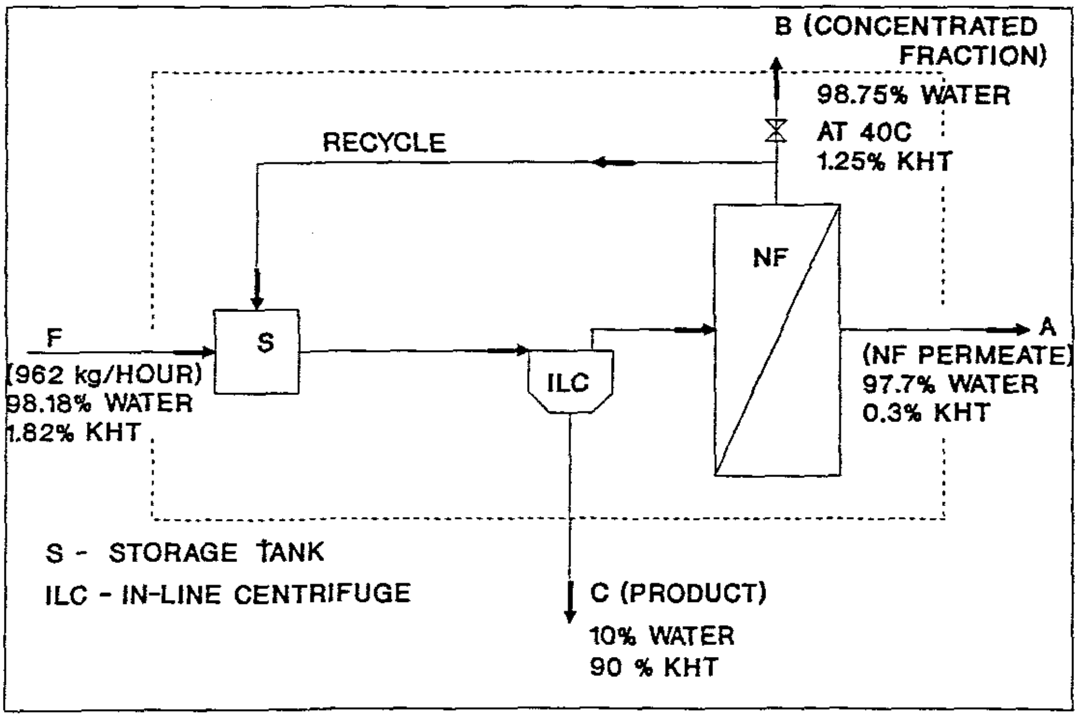


Fig. 5.17:
Nanofiltration unit.

Calculations

For 70% water recovery at A:

$$(B + C) = 0{,}3(F) = 0{,}3(962) = 288{,}6 \text{ kg/h}$$
$$A = 0{,}7(F) = 0{,}7(962) = 673{,}4 \text{ kg/h}$$

Number of modules needed in nanofiltration for average of 25 LMH and 70% recovery:

$$\text{Flux/module} = (25 \times 1{,}52 \text{ m}^2)$$
$$= 38 \ \ell/\text{h}$$

Number of modules = $A/38 = (673{,}4/38) = 18$ nanofiltration modules.

Mass balance over NF unit:

$$F = C + B + A$$
$$\therefore 962 = C + B + 673{,}4$$
$$\therefore C = (288{,}6 - B)$$

Also:

$$0{,}0182(F) = 0{,}9(C) + 0{,}0125(B) + 0{,}003(A)$$
$$\therefore 0{,}0182(962) = 0{,}9(288{,}6 - B) + 0{,}0125(B) + 0{,}003(673{,}4)$$
$$\therefore B = 275{,}2 \text{ kg/h}$$
$$\therefore C = 13{,}4 \text{ kg/h}$$

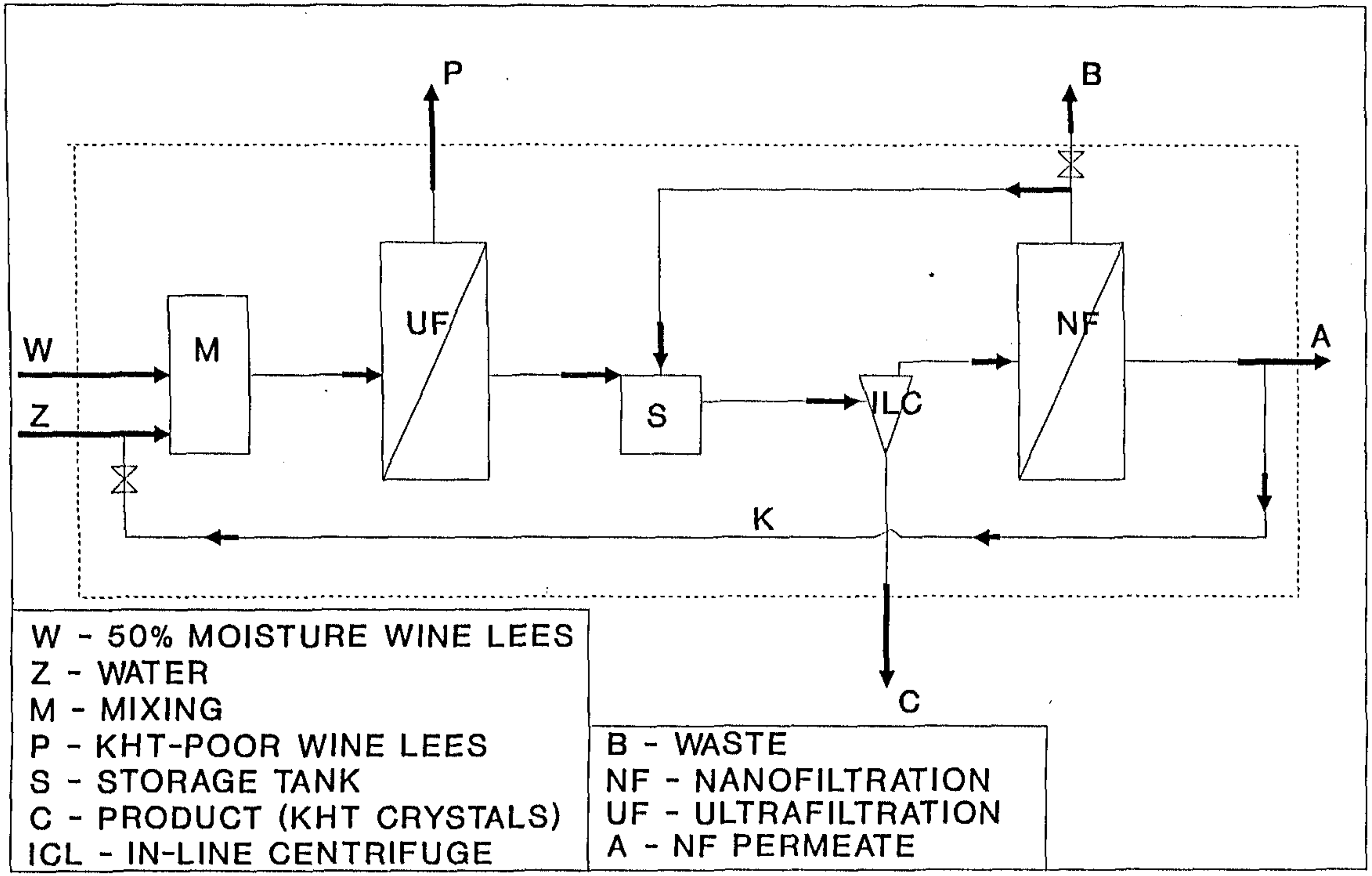


Fig. 5.18: Combination UF/NF system.

5.10 DISCUSSION

Ultrafiltration 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, to allow easy precipitation of KHT from the UF permeate during the concentration phase (with RO and NF) that followed.

The results looked promising, with permeate fluxes stabilizing within 50 h at 50 LMH. It was found that the high solids concentrations in the feed caused no visible damage to the membrane surface. It was also found that no permanent fouling occurred during the process as the membrane surface appeared clean and shiny with no organic material deposited on it. As only fresh-water washes were done during the experiments, the fact that permanent fouling did not occur, is very promising.

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 feedwater and 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 on the membrane surface or because of the affinity of KHT for yeast cells and proteins.

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 proteins through and, because of this, concentration of these proteins occurred when RO or NF were applied, resulting in a flux reduction. 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 nanofiltration CA membrane (code: 6BC84) gave the best results with fluxes more than double that of the RO membrane. The nanofiltration membranes had the added advantage of allowing undesirable salts and heavy metals to pass through the membrane, thus giving a cleaner KHT end-product.

The test results indicated the possibility of an eventual ultrafiltration/nanofiltration system. The proposed system would consist of a mixing unit, UF unit, and a nanofiltration 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 ultrafiltration unit would separate the wine lees solids and most of the proteins from the KHT in solution. The UF permeate would then enter a nanofiltration unit where concentration and subsequent precipitation of KHT would occur. One must remember that the KHT solution entering 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 the system. For this reason the best way to operate the nanofiltration 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 nanofiltration membrane test unit was therefore designed and constructed for installation at the factory at Brennochem (Figs. 5.19 and 5.20). Experimental NF membranes were assembled in a 1 m module and installed at the factory. The membranes will 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 nanofiltration field to find the most suitable membrane for this application. Modules containing different NF membranes will be installed regularly in the test unit.

An ultrafiltration 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 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 could cause blockage in the tubular membranes. For this reason it would be a good idea 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 whole operation will have to be done on a pilot-plant scale first in order to eliminate possible problems.

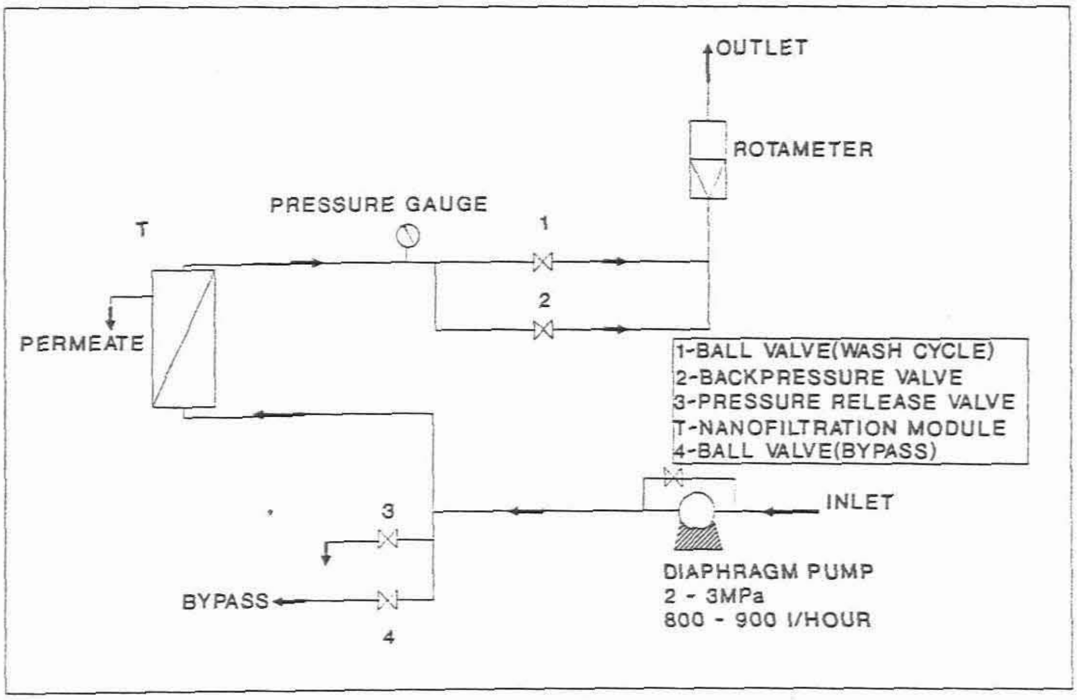


Fig. 5.19:
NF membrane test-rig design.

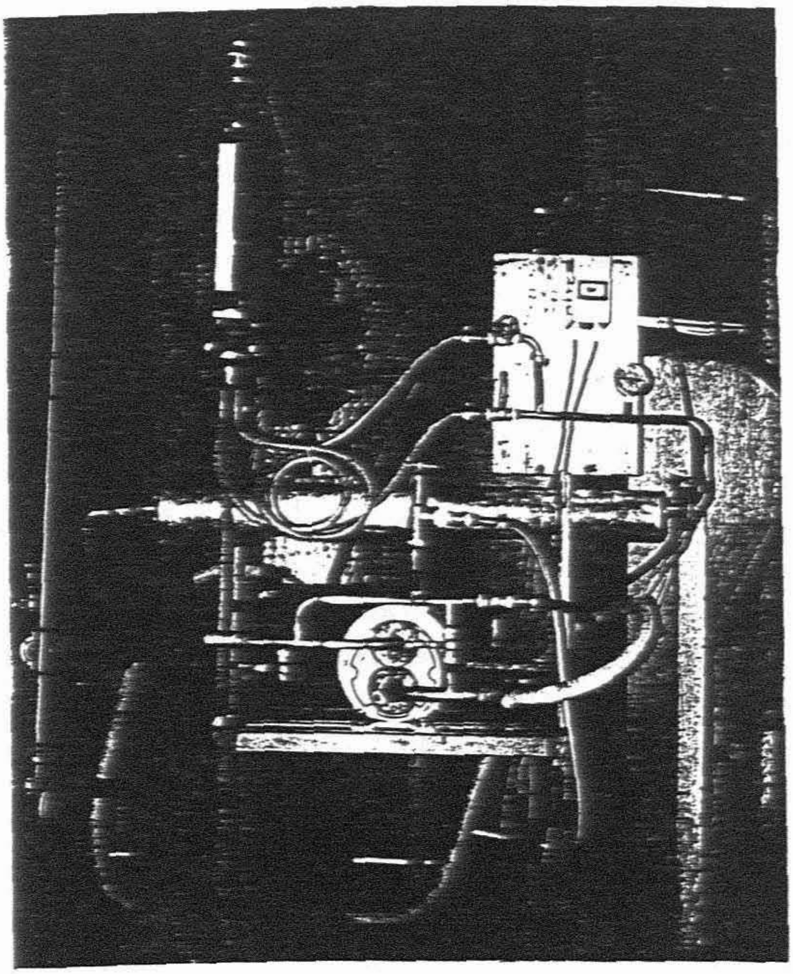


Fig. 5.20:
NF membrane test unit.

CHAPTER 6

GEL POLARIZATION AND ITS EFFECT ON MEMBRANE PERFORMANCE

6.1 INTRODUCTION

The results obtained from tests with membranes on industrial effluents, showed a flux decrease after a certain period of time. In the case of UF membranes, this flux decrease was accompanied by an unexpected salt retention. This could have been caused by different factors. However, gel polarization could possibly,be the cause of these deviations.

Gel polarization is the complication that arises when hydrocolloids (such as proteins) and other large solutes or particles are ultrafiltered. These compounds, which are largely retained by the membrane, tend to form fairly viscous and gelatinous layers on the membrane's surface. It is important to note that gel layer formation is a result of concentration polarization. Both these phenomena cause resistance to permeate flow through the membrane. Flux decline can, however, be caused by several factors other than concentration polarization and subsequent gel-layer formation.

Gel polarization is widely reported by various membrane scientists and the understanding of this phenomenon is important when considering membrane performance during operation on industrial effluents and streams. Rajnish et al. reported on the occurrence of concentration polarization when ultrafiltration was used as method of recovering inorganic chemicals from spent liquor [Ref. 6.1]. Other membrane applications where gel polarization is reported are for example the ultrafiltration of protein solutions [Ref. 6.2] and the ultrafiltration of reconstituted cheese whey [Ref. 6.3].

6.2 BACKGROUND

Blatt et al. successfully compared the qualitative features of the gel polarization model with ultrafiltration data [Ref. 6.4]. However, Fane et al. indicated that membrane properties can affect the limiting flux and they proposed a model to account for membrane heterogenity [Ref. 6.5]. Nakao et al. sampled the gel layer in the ultrafiltration of polyvinylalcohol and ovalbumin and found that the concentration of the gel layer, C_g, was not constant but increased with increasing bulk concentration and decreasing feed velocity [Ref. 6.6]. The ultrafiltration of solutions with different concentrations and fluid properties has also been considered by Kozinski and Lightfoot for constant flow to determine limiting flux [Ref. 6.7].

The flux through a membrane can be expressed as [Ref. 6.8]:

Flux = Driving force/(viscosity × total resistance)

which in the case of pressure-driven processes such as MF, UF and RO, becomes:

$$J = \Delta P/(\eta \times R_{tot}) \qquad \text{(Eq. 6.1)}$$

Various resistances contribute to the total resistance, R_{tot}. In the ideal case, only resistance offered by the membrane is involved. Because the membrane has the ability to transport one component more readily than other components, or in some cases retain solutes completely, there will be an accumulation of retained molecules near the membrane surface. The result is a highly concentrated layer accumulating on the surface of the membrane. This layer causes resistance to fluid transport. The concentration of accumulated solute molecules near the membrane surface might become so high that a gel layer might be formed which will constitute another resistance to mass transfer. With porous membranes it is possible for some solutes to penetrate membrane pores and block them, leading to pore-blocking resistance. Finally, resistance can arise due to an adsorption phenomena. This can take place on the membrane surface or within the pores themselves. This leads to rapid and sometimes even irreversible fouling of the membrane [Ref. 6.8].

Flux decline negatively influences the membrane's operation economics and therefore it is important to take the necessary precautions to combat the above-mentioned resistances. Gel polarization will be discussed in this study.

Generally, the pure-water flux through a membrane is directly proportional to the applied hydrostatic pressure (Fig. 6.1). The total resistance mentioned in equation 6.1 becomes membrane resistance, which is a constant, and depends not on the feed composition or applied pressure. However, when solutes are added to the water the behaviour in UF and MF is completely different. When the pressure is increased, the flux will increase linearly up to a point at which a limiting flux (J_{limit}) will be reached (the pressure-controlled region). Any further pressure increase will not affect the membrane flux. This region of operation is termed the mass-transfer-controlled region [Ref. 6.9]. The limiting flux depends on the concentration of the bulk feed C_b and on the mass transfer coefficient, "k", and can be expressed as:

$$J_{limit} = k \ln (C_m/C_b) \qquad \text{(Eq. 6.2)}$$

Where:

C_m = Concentration at the membrane surface.

C_b = Concentration in the bulk feed solution.

Equation 6.2 and Fig. 6.1 demonstrates that increasing the feed concentration and keeping the mass transfer coefficient and the concentration at the membrane surface constant, causes a decrease in the limiting flux. On the other hand, J_{limit} increases when the mass transfer coefficient, k, increases at constant feed concentrations. An increase in flowrate and temperature causes an increase in the mass-transfer coefficient, and subsequently the limiting flux also increases. These are important points to consider when operating conditions for pressure-driven membrane systems are investigated.

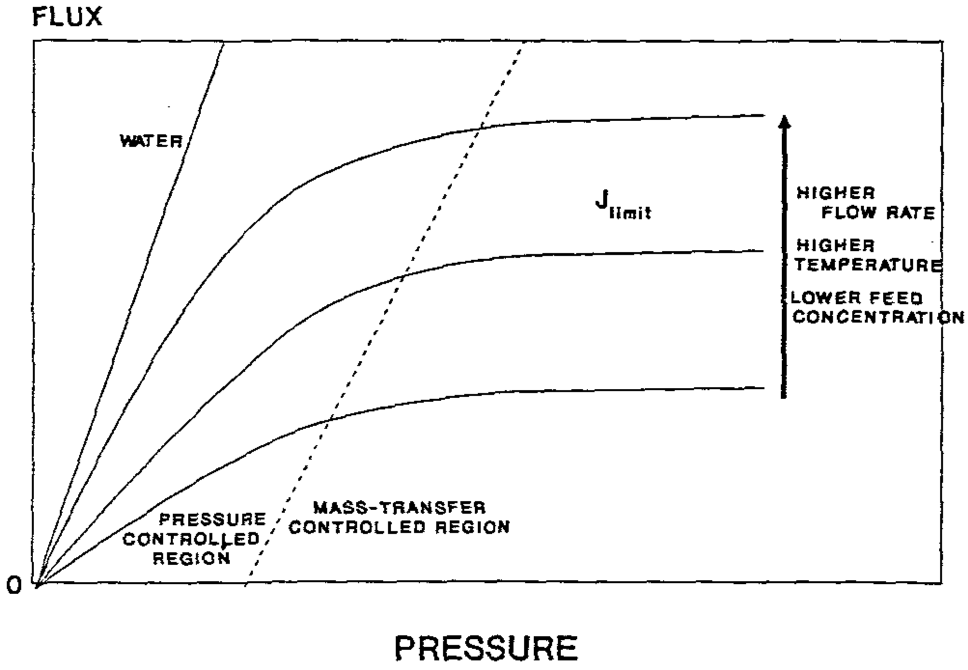


Fig. 6.1:
Pressure controlled region/ Mass transfer controlled region.

6.3 CONCENTRATION POLARIZATION

In ultrafiltration, the flux and retention are affected by concentration polarization and the formation of a gel layer or secondary resistance. Higher fluxes encountered in UF often drives the concentration at the membrane well above the solubility limit so that the filtration operation often takes place in the gel-polarized regime.

Concentration polarization is essentially the build-up of solutes close to, or on, the membrane surface. Solute is brought to the membrane surface by convective transport and solutes larger than the nominal molecular mass cut-off of the membrane are retained by the membrane, whereas solutes smaller than the membrane pores will pass freely or partially through the membrane. Because the membrane is porous, there is a continuous convective movement of the solvent (in this case water) towards the membrane surface. The macromolecular solute retained by the membrane accumulates at the membrane surface while water passes through, resulting in a concentration build-up. The solute can return to the bulk of the stream only by diffusive action. An imbalance of two opposing forces is created, namely, convective transport towards the membrane and diffusive transport away from the membrane. At steady-state, the convective flow of the solute to the membrane is equal to the diffusional backflow from the membrane to the bulk. A concentration profile is established in the boundary layer (see Figure 6.2). This phenomenon is known as concentration polarization.

6.4 GEL POLARIZATION

As mentioned before, concentration polarization can be severe in UF because of the relatively high fluxes achieved by this membrane operation (convective transport to the membrane surface), the fact that the diffusivity of macromolecules is low, and macromolecular retention is normally very high. This implies that the solute concentration at the membrane surface reaches very high levels. Under these conditions the gel concentration (C_g) of certain macromolecules may be reached, which implies that a gel layer of some sort may form on the membrane surface. Concentration polarization and gel formation are illustrated in Figure 6.2.

Gel formation is reversible, but if not closely monitored it can result in irreversible fouling. This is very important when considering membrane cleaning, because irreversible fouling can cause permanent damage to membrane performance and strict precautions have to be taken to avoid this. One of the factors that could reduce gel-layer formation is to increase the linear fluid flow velocity. When the linear velocity of the feed solution is increased, the thickness of the boundary layer (where laminar flow occurs) is reduced, and subsequently the area where concentration polarization and gel-layer formation may occur is reduced.

The gel-layer model can be used to describe the occurrence of limiting flux [Ref. 6.4, 6.10 and 6.11]. If the solute is completely retained by the membrane, the solvent flux through the membrane will increase with pressure until a critical concentration is reached, which corresponds to the gel concentration, C_g. When the pressure is increased further, the solute concentration at the membrane surface cannot exceed the gel concentration, but an increase in gel layer thickness results. This will result in an increase in gel layer resistance (R_g) so that the gel layer will eventually become the limiting factor in determining membrane flux.

In the region of limiting flux an increase in pressure leads to an increase in resistance of the gel layer, so that the net result is a constant flux. (The osmotic pressures of macromolecular molecules are neglected in this approach.) The total resistance can now be represented by the gel-layer resistance and the membrane resistance. For the gel-layer model the limiting flux can be described by:

$$J_{limit} = k \ln(C_g/C_b) \qquad \text{(Eq. 6.3)}$$

Where : C_g = gel concentration
C_b = concentration of the bulk feed.
k = mass transfer coefficient

Equation 6.3 can also be written as:

$$J_{limit} = k \ln(C_g) - k \ln(C_b) \qquad \text{(Eq. 6.4)}$$

The mass transfer coefficient, k, may also be written as [Ref. 6.12]:

$$k = D/z \qquad \text{(Eq. 6.5)}$$

Where : D = diffusion coefficient
z = thickness of the boundary layer

The mass transfer coefficient is also related to the Sherwood number (Sh) according to the Deissler correlation as follows [Ref. 6.6]:

$$\mathrm{Sh} = \frac{k\ d}{D} = 0{,}023 \times \mathrm{Re}^{0{,}875} \times \mathrm{Sc}^{0{,}25} \qquad \text{(Eq. 6.6)}$$

Where:

$$\mathrm{Re} = \frac{\rho v d}{\mu} \qquad \text{(Eq. 6.7)}$$

From Equations 6.5, 6.6 and 6.7 it can be seen that the mass transfer coefficient, k, is mainly a function of the feed flow velocity (v), the diffusion coefficient of the solute (D) and the viscosity (ρ). Of these parameters, flow velocity and viscosity are the most important [Ref. 6.8]. From Eq. 6.6 and 6.7 it can be seen that an increase in the flow velocity (v) would cause an increase in k.

Another line of argument would be that an increase in linear flow velocity would cause a decrease in the boundary layer thickness (z) and thus increase the mass transfer coefficient according to Eq. 6.5. An increase in the mass transfer coefficient would in turn cause an increase in the limiting flux (Eq. 6.4). From the above argument it is clear to see that fluid management techniques must be directed toward decreasing the boundary layer thickness, i.e., toward increasing the mass transfer coefficient k.

C_g is assumed to be constant for a given set of operating conditions and the term $k(\ln C_g)$ becomes a constant. Equation 6.4 suggests that if J_{limit} is plotted as a function of $\ln(C_b)$ the result must be a straight line of slope -k. The intercept of the straight line on the abscissa ($J_{limit} = 0$) will give the value of $\ln(C_g)$ (Fig. 6.3) [Ref. 6.8].

For concentrated solutions, after precipitation of gel, the concentration at the membrane is fixed and passage of solute occurs at a constant rate. Unfortunately, binary solutions do not always behave in this way. For example, the pharmaceutical industry is keenly interested in having a UF membrane capable of fractionating albumin/globulin mixtures, and there are, in fact, membranes that offer better than 95% retention of gamma globulin and less than 10% retention of albumin. However, the presence of small amounts of gamma globulin causes formation of a gel layer on the membrane that retains the smaller albumin molecule. This gel layer limits the ability of the membrane to fractionate various proteins [Ref. 6.12].

Sasol cooling-water blowdown effluent was used in this study in order to determine whether:

(i) a gel layer forms on the membrane surface;
(ii) it is possible to predict the flux according to the gel-layer model; and
(iii) the concentration of the gel layer.

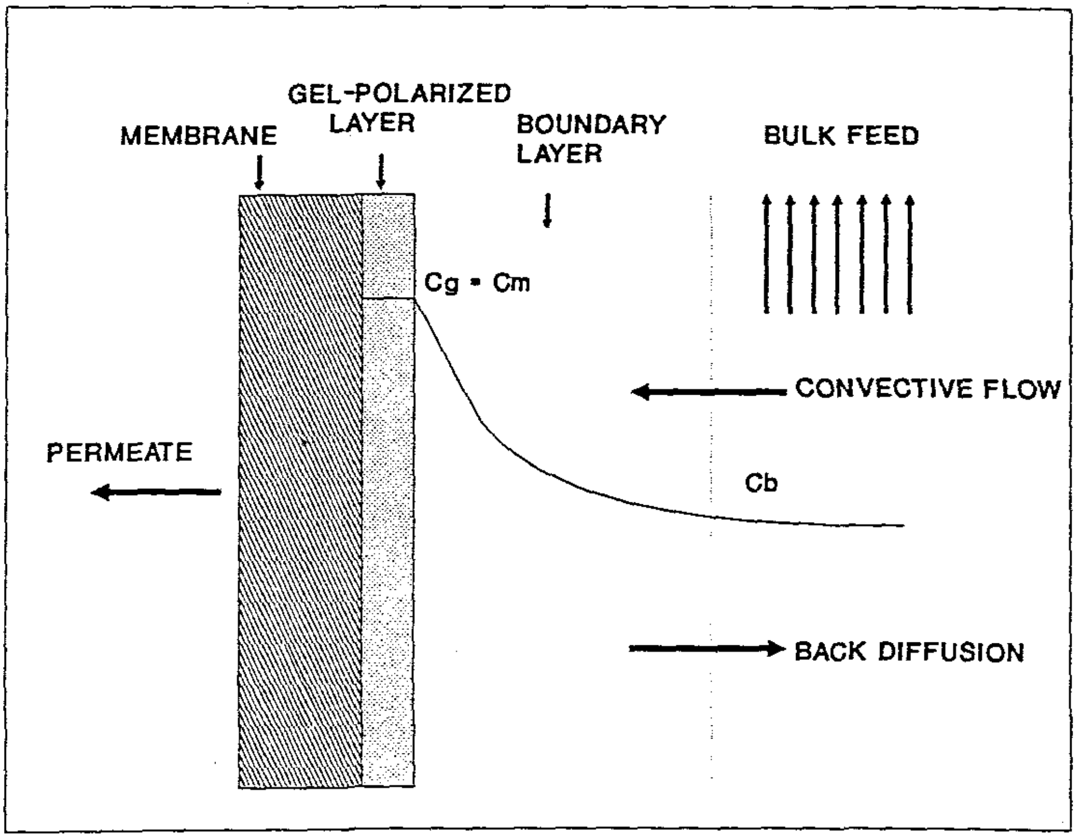


Fig. 6.2:
Concentration polarization and gel-layer formation.

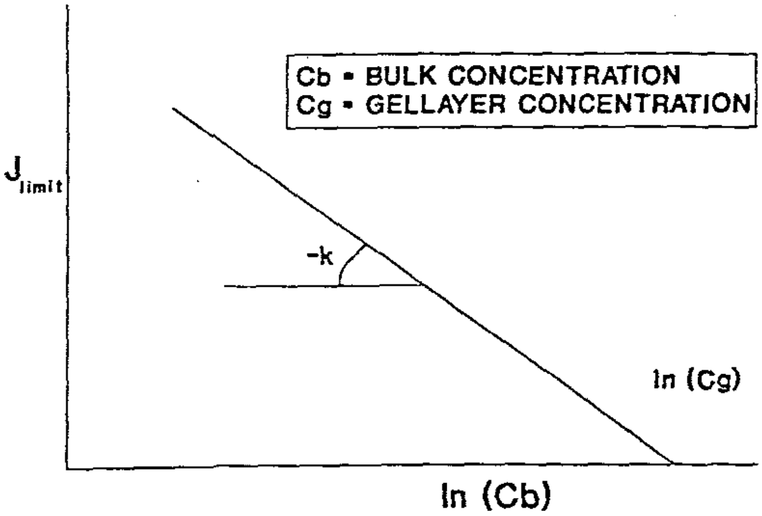


Fig. 6.3:
Limiting flux as a function of the logarithm of the bulk feed concentration.

6.5 THE EXISTENCE OF A GEL LAYER

During past tests on Sasol cooling-water blowdown, it became evident that some ultrafiltration membrane fluxes dropped drastically in the first few hours of operation. After approximately 100 h of operation the membrane fluxes stabilized. Another interesting fact was that the UF membranes sometimes rejected up to 10% of the salts present in the system (Fig. 6.4 and 6.5). These results indicated gel polarization. A study of the membrane surface after 1 200 h of operation revealed a dark-brown gelatinous layer on the membrane surface (Fig. 6.6). This layer could easily be removed by mechanical (e.g. sponge-balls) or non-mechanical means (e.g. soap washes).

Results of tests conducted on nanofiltration membranes also pointed to the existence of a gel-polarized layer. It must be remembered that the flux through a NF membrane is lower than that through an UF membrane. The result of a lower membrane flux could be a thinner gel-polarized layer, because equilibrium is more readily established. In other words, the two opposing forces, namely, convective flux towards the membrane and diffusive action away from the membrane, will produce equilibrium at an earlier stage. In the case of NF membranes, flux stabilization should therefore occur at an earlier stage. This is shown very clearly in Figure 6.7. Three experimental NF membranes were tested on the effluent. (Figs. 6.7 and 6.8) NF membrane test results illustrate the above point very clearly. The experimental membrane is marked "X". This membrane had a higher initial flux (and lower retention) than the other two membranes. However, it took a considerable time for the membrane flux to stabilize and eventually the flux stabilized at a lower value than those of the other membranes.

The facts in the above discussion pointed to the existence of a gel layer on the membrane surface. Further tests were required to determine whether it was possible to predict flux according to the gel-layer model.

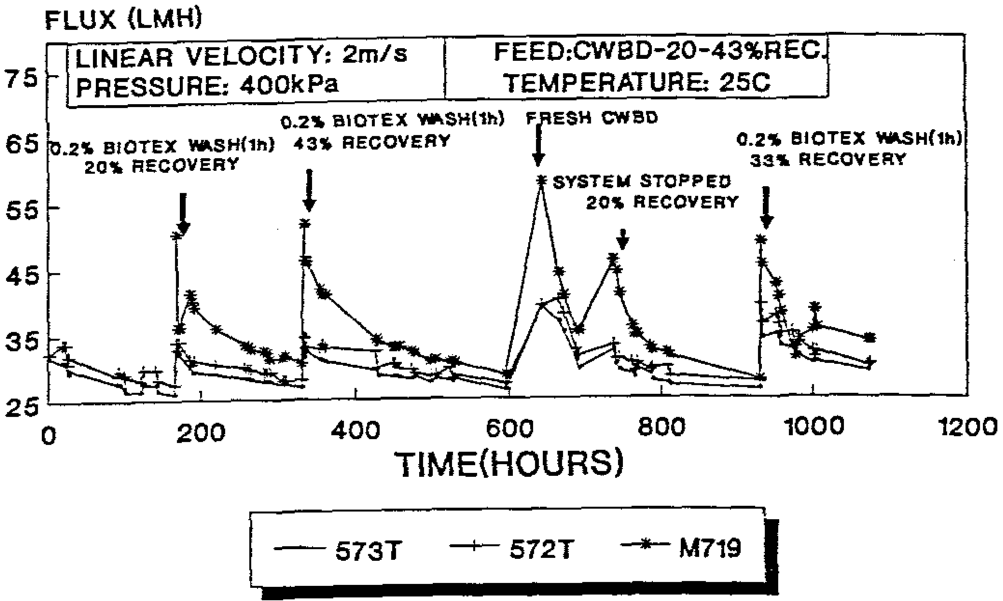


Fig. 6.4:

Flux performance of different UF membranes operated on CWBD.

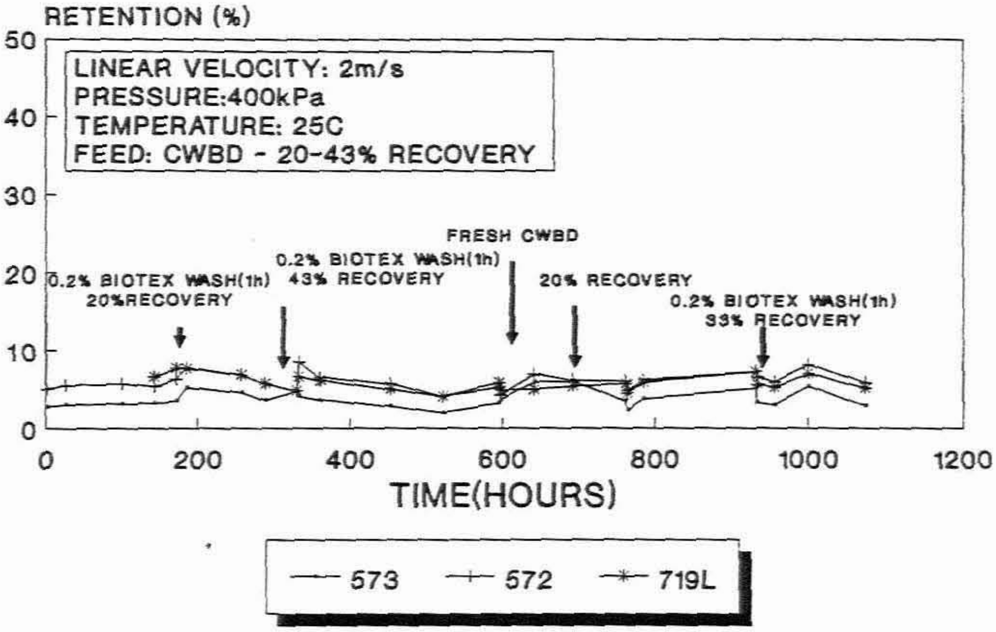


Fig. 6.5:
Retention performance of different UF membranes operated on CWBD.

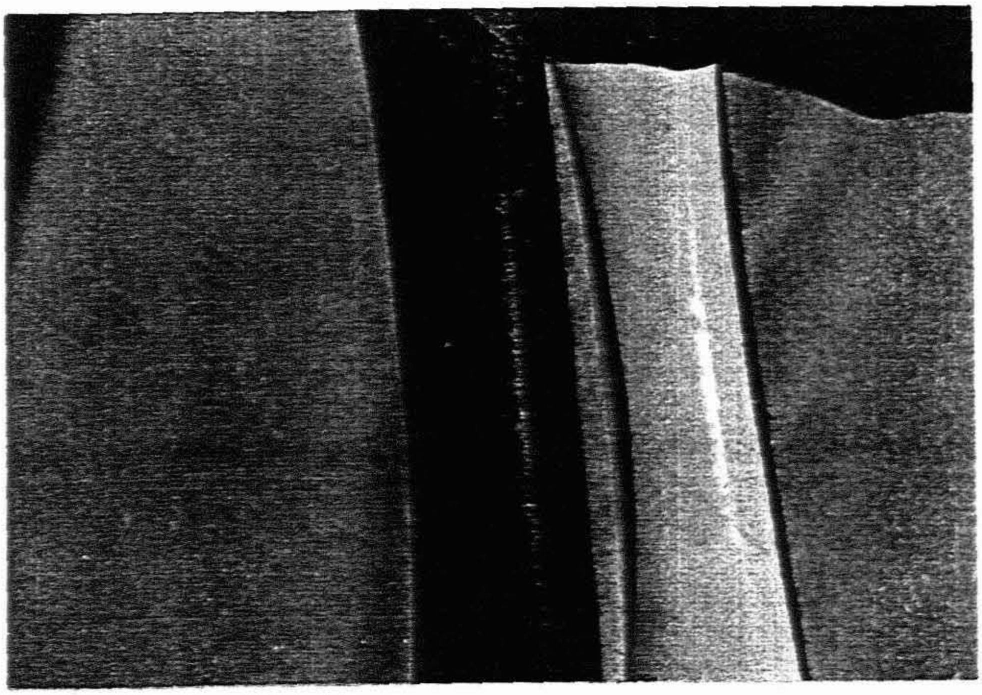


Fig. 6.6:
Gel-layer visible on UF membrane surface.

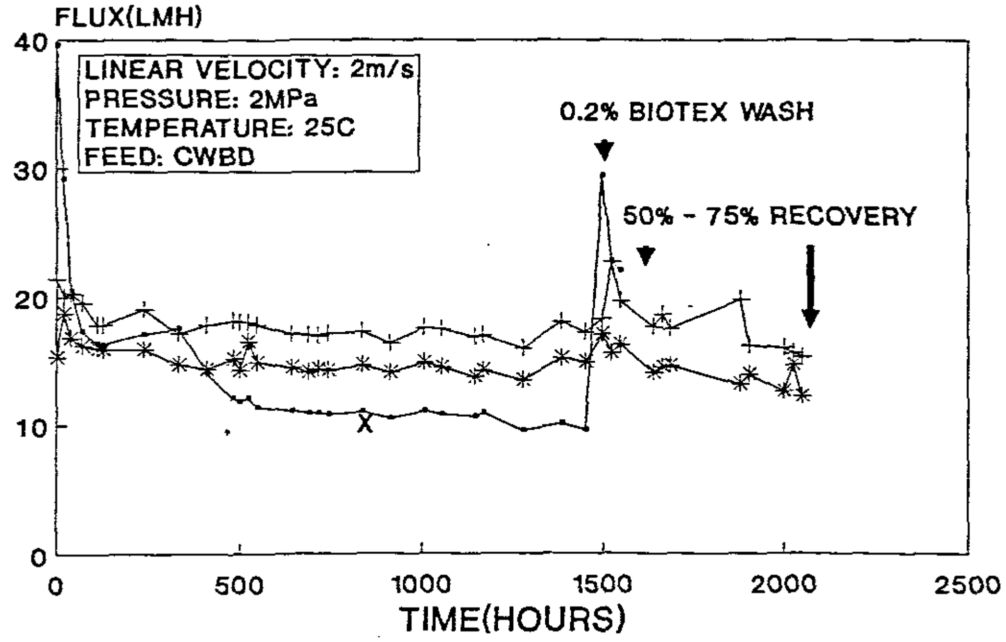


Fig. 6.7:
Flux performance of different experimental NF membranes operated on CWBD.

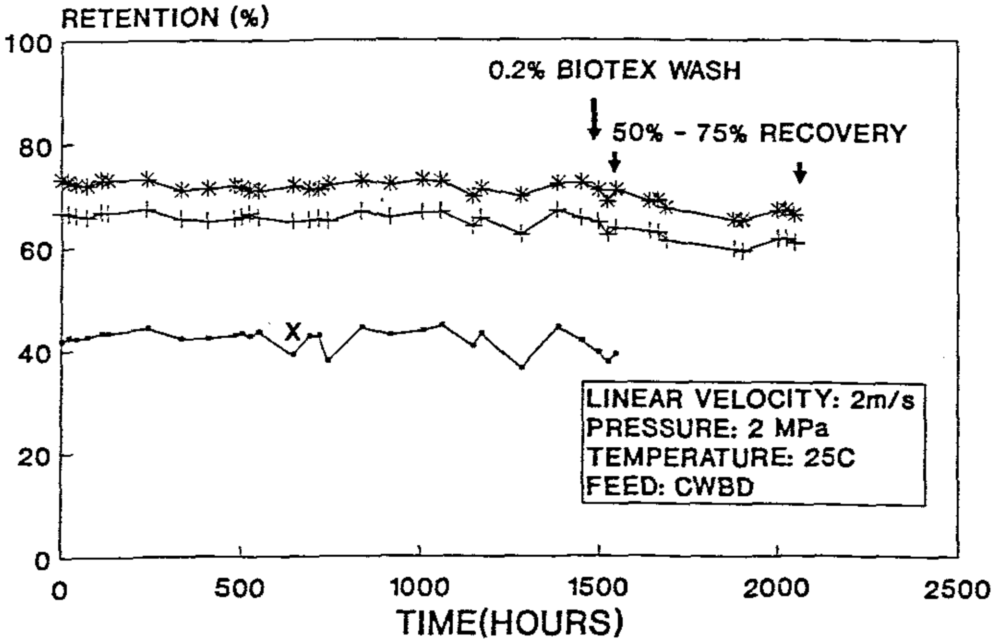


Fig. 6.8:
Retention performance of different experimental NF membranes operated on CWBD.

6.6 FLUX PREDICTION ACCORDING TO THE GEL-LAYER MODEL

In the tests described below, an established UF membrane (code 719) was used. Six tubular membranes were tested at different concentrations. After each test at a certain concentration, a thorough soap wash was done to ensure that no external factors could influence the results. Percentage recovery was used as a term to describe degree of concentration. The membranes were first tested at different recoveries of 0%, 20%, 40%, 55% and 70%. As shown in Figure 6.9 the flux decreased as the concentration was increased. At 400 kPa the membrane flux was still in the pressure-controlled region (see Fig. 6.10).

The limiting flux (J_{limit}) of the membranes could now be determined at different concentrations. These tests were conducted at 0%, 50% and 70% recovery (Fig. 6.10). Typical flux-pressure curves were obtained at the different concentrations. The results obtained were the average of six UF membranes. The limiting fluxes at the different concentrations were found to be :

0% Recovery - 105 LMH
50% Recovery - 75 LMH
70% Recovery - 61 LMH

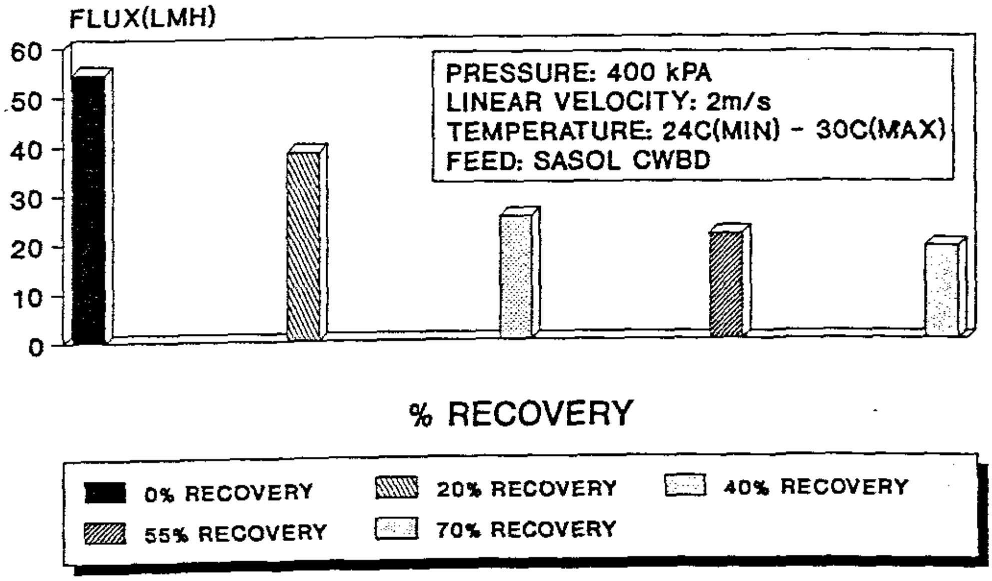


Fig. 6.9:
Flux of UF membrane 719 as a function of percentage recovery.

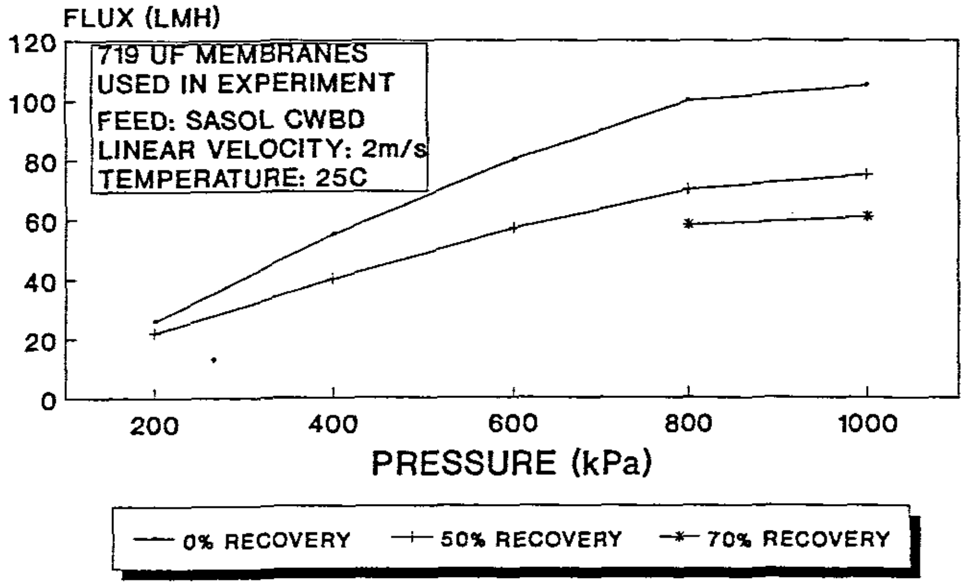


Fig. 6.10:
Limiting flux determination.

It should be stressed that the UF membranes did not retain all the dissolved solids in the effluent. Most of the retained material was suspended solids. The concentration of suspended solids was therefore regarded as the only valid value that could be used in determining the gel-layer concentration. It was assumed therefore that the suspended solids were the only "ingredient" of the gel layer.

However, it was known that 719 UF membranes had a 21% COD retention. Analysis of feedwater showed that these membranes retained 72% Ca^{2+} (possibly as CaO or $CaSO_4$) and 84% Fe_2O_3 (see Chapter 4). These compounds could therefore be considered to play a role in gel-layer formation. Another factor that was not taken into account was that certain solutes (eg. SiO_2, AlO_3 and sulphates) could precipitate on the membrane surface due to high concentrations in the boundary layer. It can however be argued that suspended solids played a dominant role because they made up a large percentage of the total solids in the effluent and a 100% retention of suspended solids and organic material occurred when the membrane was tested on the effluent.

The limiting fluxes (transformed from LMH to m/s) at 0%, 50% and 70% recovery were plotted against the log of the concentration of the bulk stream (ln C_b). Figure 6.11 shows that by extrapolating the straight line to the X-axis, ln(C_g) could be obtained. From this the gel-layer concentration (C_g) was found to be 15,64 kg/m^3. Using Equation 6.3, the mass transfer coefficient could be determined.

$$J_{limit} = k\ \ln(C_g/C_b)$$

At 0% Recovery:

$$\begin{aligned} k &= J_{limit}/\{\ln(C_g/C_b)\} \\ &= (3\times E-5)/\{\ln(15,64/1,633)\} \\ &= 1,33\times E-5\ m/s \end{aligned}$$

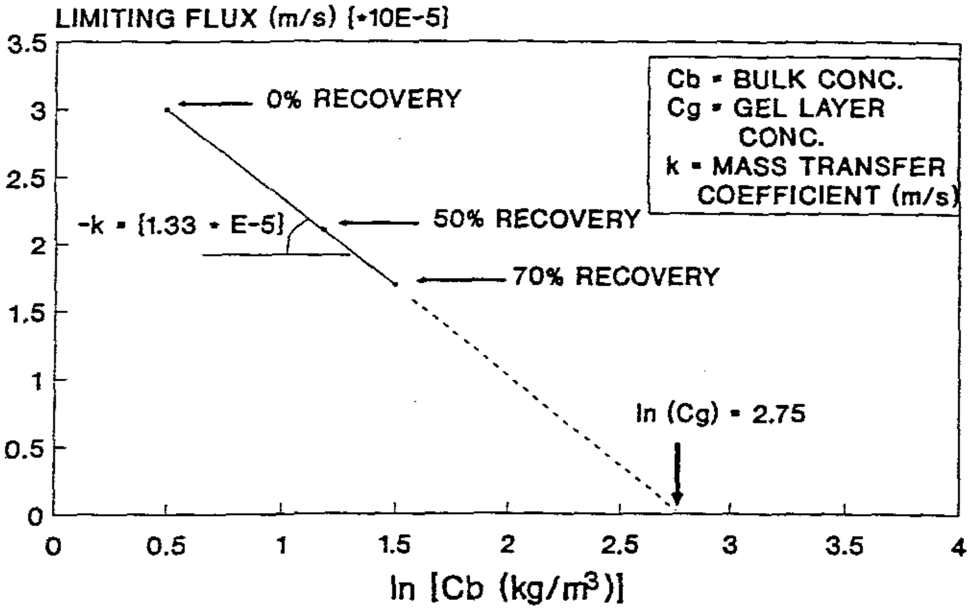


Fig. 6.11:

Determination of gel concentration (C_g) and mass transfer coefficient (k).

Because C_g and k are constant under specific conditions (linear velocity, temperature), the limiting flux could be predicted for different feed concentrations by means of equation 6.3. It must, however, be stressed that this is one model of many and that it has certain shortcomings, such as the fact that it does not take into account the effect of compaction of the membrane and that it assumes that the osmotic pressure of macromolecules is negligible. It can, however, be used as a guideline for flux predictions if certain variables are known.

6.7 DISCUSSION

This study showed that the limiting flux of an industrial effluent can be predicted by using the gel-layer model. This information could be valuable in the design of an ultrafiltration plant for a specific industry.

Gel polarization is a reversible phenomenon which means that the original fresh-water flux could be re-established after a soap wash or, in some cases, even a fresh-water flush. However, in practice a continuous decline in flux is often observed. Such continuous flux decline is the result of membrane fouling, which may be defined as the irreversible deposition of retained particles, colloids, suspensions, macromolecules, etc. on or in the membrane structure. Permanent membrane fouling may be the result of adsorption of foulants on the membrane surface, plugging of foulants in the membrane pore structure, precipitation of solutes and compaction of the gel layer. Although certain methods to combat fouling exists, the golden rule is still that prevention is better than cure.

Methods for reducing fouling are:

(i) Cleaning methods - Constant observation is required to make cleaning methods effective. The frequency with which membranes must be cleaned can be estimated from process optimization. Three cleaning methods can be distinguished:

    (i) hydraulic cleaning (e.g. high velocity water flush, flow reversal);
    (ii) mechanical cleaning (e.g. sponge-balls); and
    (iii) chemical cleaning (e.g. soap washes, enzymes)

(ii) Pretreatment of the feed solution, e.g. pH adjustment, chlorination, chemical clarification, adsorption onto activated carbon.

(iii) Membrane properties - it is important to select a membrane with properties which suit the application. For example, a small pore size could reduce fouling in applications where the foulants are of relatively small molecular mass.

(iv) Module and process conditions - Fouling decreases as concentration polarization decreases. Concentration polarization and subsequent fouling can be reduced by increasing the mass transfer coefficient. This can be achieved by, for example, increasing the flow velocity and by lowering operating pressures. Low-flux membranes could also be used to combat concentration polarization [Ref. 6.8].

CHAPTER 7

CONCLUSION

7.1 FABRICATION OF UTF RO MEMBRANES FOR BRACKWATER TREATMENT

Tubular ultra-thin-film RO membranes were manufactured for on-site testing in Botswana. The objective of the operation was to desalinate brackish water to give a potable water which would comply with certain standards. The standards with which the membranes were to comply were that the membranes should have a NaCl retention of above 90% and be able to operate at relatively low pressures of between 2 and 3 MPa. The membranes had to be potted in modules by Membratek before installation at the site in Botswana.

The experimental UTF-RO CAMOH and CAMPIP membranes had been previously manufactured and tested only as flat-sheet membranes. These membranes were manufactured for the first time in the tubular configuration. The membranes were first manufactured on a laboratory-scale to determine whether the membrane product met the desired standards. The best performing membranes were selected for manufacture on a larger scale.

The selected membranes, produced on a larger scale, were stored in a weak formaldehyde solution prior having it sent to Membratek for incorporation into modules. Unfortunately the test results obtained with the potted membranes did not meet the desired standards. Later tests performed on controls and membranes taken from the modules suggested that the membranes were most probably damaged during the potting operation.

A UTF-RO membrane consists of a thin and relatively brittle membrane layer on a substrate UF 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 would cause membrane performance to deteriorate. Other possible reasons for the poor performance of the these membranes after the module-making process may have been:

(i) inadequate storing methods;
(ii) the membranes could have dried out during the module-making process (embrittlement).

It is clear that research needs to be done to establish methods of storing these membranes, and to minimize damage during assembly and fabrication into modules.

The membranes manufactured for this application were, however, successfully used in other applications (e.g. Sasol), when operated in a single-cell configuration.

7.2 MEMBRANE APPLICATIONS ON SASOL COOLING-WATER BLOWDOWN

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

Experimental UF and RO membranes were tested on SASOL cooling-water blowdown. Various industrial effluents have different chemical compositions and therefore exhibit different properties. In the case of this particular effluent, the challenge to recover water using pressure-driven membrane systems, 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 membrane surfaces. Permanent fouling could fortunately be prevented by means of regular soap washes.

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

CWBD was sent regularly to Stellenbosch in 200ℓ drums. Various membranes were tested on this effluent. After extensive testing of tubular UF, capillary UF and PVOH nanofiltration 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.

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 proved 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% suspended solids and close to 100% colour removal was achieved by ultrafiltration. 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 achieve higher average fluxes. 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 nanofiltration, the biggest problem proved to be the relatively rapid, although not permanent, fouling of the membranes. A general conductivity retention of approximately 70% and a 99% PO_4^{3-}, SO_4^{2-} and colour retention were achieved in the case of 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%. Again, the main cause 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.

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

7.3 THE REMOVAL OF POTASSIUM BITARTRATE FROM WINE RESTS WITH PRESSURE-DRIVEN MEMBRANES

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 reverse osmosis or nanofiltration 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 nanofiltration membranes. An experimental nanofiltration membrane gave good fluxes with KHT retentions of above 80%. The nanofiltration membrane had the added advantage when compared with RO in that it allowed dissolved salts and heavy metal ions to pass through, while retaining the KHT molecules.

A nanofiltration 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 will 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.

Various tests still need to be conducted in the nanofiltration field to find the most suitable membrane for this application. Modules containing different NF membranes will be installed regularly in the test unit.

An ultrafiltration test unit should also be installed at the factory and at a later stage be operated in conjunction with the existing NF unit. The whole operation will have to be done first on a pilot-plant scale in order to eliminate possible problems.

7.4 GEL POLARIZATION AND ITS EFFECT ON MEMBRANE PERFORMANCE

A study was done to determine the effect of gel-layer formation on membrane performance. The results obtained from tests on the membranes on industrial effluents, showed that there was a flux decrease after a certain period of time. In the case of UF membranes, this flux decrease was coupled with an unexpected salt retention. This could have been the result of a variety of factors. However, gel polarization could possibly be the cause of these deviations.

Sasol cooling-water blowdown effluent was used in the case study. The object of the study was to determine:

(i) if a gel layer forms on the membrane surface;
(ii) the concentration of the gel layer; and
(iii) if it is possible to predict the flux according to the gel-layer model.

After various tests were conducted, the existence of a gel layer was confirmed. Limiting flux could be predicted for different feed concentrations by means of the gel-layer model. It must be stressed that this is one model of many and that it has certain shortcomings. It can, however, be used as a guideline for flux predictions.

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