INVESTIGATION TO UPGRADE SECONDARY TREATED SEWAGE EFFLUENT BY MEANS OF ULTRAFILTRATION AND NANOFILTRATION FOR MUNICIPAL AND INDUSTRIAL USE

Final Report to the

Water Research Commission

by

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The work to evaluate the experimental capillary membranes and module systems on secondary treated sewage effluent would not have been possible without the cooperation of the **Uitenhage Municipality**. The contributions of the Municipality towards the successful completion of the work is sincerely appreciated.

The various contributions of members of the staff at the sewage works is also appreciated. We are also thankful for the assistance of the laboratory staff at the sewage works with sample analysis. The work of **Ms HC Kleinhans**, in particular, has found its way into many of the tables and figures presented in the report.

Executive Summary

Objectives

The objectives of the research were to determine to what extent medium-molecular-mass cut-off capillary ultrafiltration and tubular nanofiltration membranes, developed at the Institute of Polymer Science of the University of Stellenbosch, could be used to improve the quality of secondary treated sewage and water from the Orange/Fish River scheme. It was not intended to develop a membrane-treatment process, but rather to evaluate the performance and integrity of the nanofiltration membranes and capillary membranes and modules over an extended period of operation, under specific operating conditions.

Objectives not addressed

According to the original contract, the ultrafiltration and nanofiltration membranes and modules were to be tested on secondary-treated sewage as well as on Orange River water. At the time that the contract proposals were submitted, concern was being expressed by Uitenhage industrialists regarding the hardness and colour content of the Orange River water delivered to Uitenhage via the Fish River Tunnel scheme. The initial problem with regards to hardness and colour improved considerably and was found more acceptable once water was drawn continuously from the Orange River Scheme and, after treatment, was blended with indigeneous water. This made treatment by means of ultrafiltration and nanofiltration unecessary and resulted in neither of the membrane processes being tested on Orange River water.

However, this did not detract from the need to assess ultrafiltration as a possible one-step treatment operation to clarify and purify surface water to standards set for potable water.

The opportunity to test the capillary membrane ultrafiltration process on surface water arose at Mon Villa (the then seminar centre of the University of Stellenbosch), whose only consistent source of water was irrigation water from the Theewaterskloof/Helderberg irrigation scheme (WRC project KV/184: *Research on rural and peri-urban water supply).*

This programme showed over a period of more than 20 000h that capillary ultrafiltration membranes can be used to provide high-quality drinking water in a one-step operation without the addition of chemicals.

Because of the limited membrane area and feed-tank holding volumes of the bench-scale membrane plants at Uitenhage, problems arose with heat build-up during recirculation. Recovery ratios had therefore to be kept low during the experiments at Uitenhage. (This problem was overcome at the Mon Villa site where a 4 500l feed tank and much larger membrane capacity was installed. Recovery ratios exceeding 95% were regularly achieved during those experiments, without any permanent loss in membrane flux performance).

Membranes and modules

The capillary membranes and modules which were to be tested were the research products of WRC Project No. 387 entitled: *The development and production of membrane systems.* The ultrafiltration capillary membranes (coded #748) that were developed during this research programme were fabricated from poly(ether sulphone). The membranes had a molecular-mass cut-off of 35 000 dalton (tested on polyethylene glycol) and were internally skinned. Two module prototypes were developed during WRC Project No. 387 to house the capillary membranes. The one module, a 40mm-diameter cartridge-type module with a transparent uPVC shroud, was secured in a manifold fabricated from standard uPVC T-pieces and sealed by means of O-rings. The other, a 50mm module with a stainless steel shroud, was flange-mounted.

The tubular cellulose acetate membranes which were to be tested were also the research products of WRC Project No. 387. These membranes were housed in PCI modules. The modules were fitted with perforated stainless steel tubes and sealed on either side with rubber grommets. Eighteen 2,4m-long membranes were connected in series in each of these modules.

CONCLUSIONS

- The ultrafiltration capillary and nanofiltration tubular membranes performed well during the studies and no problems were experienced with their integrity over the 16 000h period tested.

- The turbidity of the ultrafiltered product was very low. The membranes showed good colour-removal capabilities, but the colour of the filtered product was still higher than the maximum specified for potable water.

- The COD load in the ultrafiltered product was low, but not as low as that in the nanofiltered product.

- The flux performances of the 40mm and 50mm modules did not correspond. The membranes were produced from the same formulation, but the fabrication protocol was slightly different. It should therefore be possible to improve the flux performance of the capillary membranes, without decreasing the retention performance, by modifying the membrane formulation and fabrication protocol.

- The 40mm capillary membrane cartridge modules performed well. No leaks occurred between the tubesheet and the module shroud as the seal remained intact. The design of the 50mm stainless steel capillary membrane cartridge module also proved to be adequate to sustain long-term use.

- The stainless steel shroud of the 50mm module proved to be an advantage as no algal growth appeared on these membranes, as happened to the 40mm modules which had transparent shrouds.

- u-PVC proved to be an adequate and inexpensive material for use in the construction of module shrouds. However, the u-PVC material did impose an upper operating temperature limit of 40°C.

- The performance of the nanofiltration membranes declined with time. This was ascribed to hydrolysis of the cellulose acetate membranes as no acid was used to adjust the pH of the feed water to a more suitable level.

- The quality of the nanofiltered water was very high, and nanofiltration could be useful for the treatment of secondary treated sewage, to produce high quality water for industrial use.

RECOMMENDATIONS

The capillary ultrafiltration membranes performed well during the experiments and their relevance in potable water production and effluent treatment should be investigated further. There are, however, aspects of the present technology that should receive attention. These are summarized below:

- Membrane fouling could be a deterent in the use of membrane filtration technology. The development of *antifouling* precoats should be investigated as it would not only ~~shorten~~ lengthen intervals between membrane cleaning, but would also reduce the harshness of the protocol required to clean the membranes. This applies equally to nanofiltration and ultrafiltration.

- Low-cost modules and manifolding should be developed. Special attention should be given to increasing the membrane area in these modules. The modules and manifolding system should be designed so as to simplify module removal for ease of membrane replacement and other reasons.

- The use of ultrafiltration to upgrade industrial effluents should be investigated on a larger scale (20 to 40m^2 membrane area).

- The use of ultrafiltration to upgrade surface water to standards set for drinking water should be investigated on a larger scale. The possibility of using a standard approach to the treatment of waters with different turbidities should be investigated. It is very important that indicator micro-organisms should be monitored very regularly during such experiments so as to determine the efficiency of the membranes as absolute filtration barriers.

- Attention should be given to the development of a standardized microbial or virus indicator test to monitor the removal/reduction efficiency of ultrafiltration membranes in potable water production applications or as a quality control measure during membrane manufacture.

- A cost study should be conducted to determine the specific cost to treat surface water to drinking water standards.

TECHNOLOGY TRANSFER

The results obtained in this study indicated that the capillary ultrafiltration membranes and module prototypes developed at the Institute of Polymer Science were useful for water clarification and colour reduction. As an extention of the work conducted in this programme, the ultrafiltration membranes were tested in larger-sized modules at Mon Villa (WRC project KV/184: *Research on rural and peri-urban water supply*). The 90mm modules used had a membrane area of $4m^2$ and were an upscaled version of the 40mm module design tested at Uitenhage. The inlet and outlet manifolds of the 90mm modules had similar T-piece designs similar to those used at Uitenhage.

The results of the trials at Mon Villa demonstrated the usefulness of ultrafiltration capillary membranes as a one-step treatment option for potable water production. The raw water treated at Mon Villa had an incoming colour content that ranged between 40 and 60 Hazen units. A surprising result was that the membranes were capable of producing a final water with a colour content below 5 Hazen. These results lead to further investigations and in a collaborative WRC programme (WRC project K5/764: *Research into water supply to rural and peri-urban communities using membrane technologies*), which involved co-operation from the Chemical Engineering Department of ML Sultan Technikon, it was demonstrated, at Suurbraak in the South Cape, that the membrane process was capable of reducing the colour content of the incoming water from Hazen colour units of as high 600 to values of below 10. The water recovery ratios achieved at Suurbraak often exceeded 85%, and in which case the concentrate had colour values exceeding 2000 Hazen units.

A pilot plant operating on six 90mm capillary ultrafiltration membrane modules is currently being tested at the Windhoek Goreangab reclamation plant, to determine the capability of the membranes to remove protozoan cysts and o-ocysts from the reclaimed water. The membranes are producing good quality water, with turbidity values often as low as 0,06 NTU.

Although the ultrafiltration process is still under development and much R&D is essential to improve the membranes, modules and process, Umgeni Water has expressed an interest in commercializing the technology. A pilot plant which can acommodate up to twelve 90mm

modules has been constructed by Umgeni Water, in collaboration with the Chemical Engineering Department of ML Sultan Technikon, to test the process on various feed waters.

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I. INTRODUCTION

Water is a scarce and precious commodity in Southern Africa. In many parts of this region the available surface and subsurface resources are nearly, or are already being, exploited to capacity. In certain areas water is being redirected from one catchment area to supplement that in another, whereas in others, for example Windhoek in Namibia, secondary treated sewage is recovered to augment available supplies. A treatment technology was developed in Windhoek by which the quality of the sewage that was treated by conventional technology could be upgraded to comply with standards for potable water. Small quantities of this water are recycled for domestic and drinking purposes.

The Eastern Cape is often faced with droughts and consequently with serious water-shortage problems. This problem has been overcome to some extent by diverting water by tunnel from the Orange River to the Fish River to augment regional supplies. The Cape Peninsula is faced with another problem. Because of the rate of urbanization and the limited number of sites available for construction of dams, serious water shortages are forecast for the region in the short term, with little alternative but to turn to unconventional resources in the longer term. Sea water desalination offers one possibility for providing potable water; another is to use tertiary treated domestic sewage for industrial and domestic applications.

No technology has been implemented in Southern Africa or elsewhere to recover high percentages of secondary treated sewage to provide high quality water for potable use. In this regard membrane filtration could provide another technological option for improving the quality of secondary treated sewage to a stage at which larger volumes of municipal effluent could be recycled.

Different cross-flow pressure-driven membrane processes fulfill different functions. Microfiltration membranes remove suspended solids and reduce bacteriological activity, but will not reduce the colour or dissolved organic content of the water. Ultrafiltration, in which a finer membrane filter is used, will remove medium-molecular-mass dissolved organics and reduce turbidity to levels of 0,1NTU, but can not desalinate water. Nanofiltration membranes

which are even finer can partly desalinate water (soften it, so to speak) and remove substantial quantities of low-molecular-mass organic materials as well as viruses. However, reverse osmosis can be used to produce higher quality filtrates by the use of increased operating or driving pressures to effect separation. Table 1 gives some indication of operating pressure ranges for these pressure-driven membrane processes.

Table 1: Lower operating pressure limits for pressure-driven membrane operations

Microfiltration	Ultrafiltration	Nanofiltration	Reverse osmosis
0,2 bar	1 bar	5 bar	10 bar

II. SCOPE

Two newly developed membrane systems were evaluated in an application to improve the quality of secondary treated sewage effluent from the Uitenhage treatment works. The membrane plants drew their water from the maturation pond. The membranes would furthermore be operated under conditions of limited pretreatment

- An important aspect of the work was to determine the durability and integrity of the poly(ether sulphone) ultrafiltration capillary membranes that were developed for the purpose, and to reach some conclusion about the life-expectancy of these membranes. Various ultrafiltration module and manifold configurations were also evaluated with a view to directing future research and development of larger-sized modules.
- It was also important to obtain some knowledge regarding the operability of the membranes on maturation-pond waters. The performance of tubular cellulose acetate nanofiltration (NF) membranes was to be evaluated over an extended period of time in order to determine performance data and fouling tendencies.
- *Biotex* is often recommended as a useful detergent for cleaning fouled membranes, but it is not supplied in bulk. Another detergent that is available in bulk quantities was evaluated as an alternative cleaning reagent for cellulose acetate nanofiltration membranes.

1. WATER BALANCE AT UITENHAGE

Uitenhage draws its water from three main sources: the Groendal dam, natural springs and the Orange River via the Fish River Tunnel. The latter water is treated by Port Elizabeth Municipality (PEM) before it is distributed to Uitenhage. The water from the Groendal dam and springs is treated by the Uitenhage Municipality. Table 2 gives an approximate indication of water consumption rates over a period of six years, and Table 3 gives an

approximate indication of the volume of water returned to the sewage works during wet and dry periods. A total of 1Ml/d treated sewage is presently being used to irrigate sportsfields and by industry as cooling water.

Uitenhage has a diversity of industries ranging from motorcar manufacture to the fabrication of export-quality knitwear. These industries are placed under severe pressure to reduce their water consumption during periods of severe drought which appear to come in 10-year cycles, (see Figure 1). Larger volumes of water may be drawn by way of Port Elizabeth Municipality from the Fish River scheme, but from the analysis shown in Table 4 it can be deduced that the quality of this water is lower than that of water from indigenous resources. Industry will therefore be forced during periods of severe drought to introduce point-source treatment, such as water softening, before the water can be used. If this happens, an alternative would be to re-use secondary treated sewage.

Table 2: Comparison of Uitenhage water consumption rates (annual)

Water source	90/91	91/92	92/93	93/94	94/95	95/96
			Daily Average in Ml			
Groendal dam	11.34	6.91	8.88	10.14	10.25	10.99
Natural springs	4.03	3.87	3.86	4.02	4.29	4.5
PEM (Orange river)	6.23	5.32	3.44	3.09	3.21	1.61
Total	21.6	16.1	16.18	17.25	17.75	17.1

Table 3: Effluent returned to the sewage works for treatment

Effluent source	Normal conditions	Dry conditions
	Ml/day	
Industries	8	6
Domestic (Uitenhage)	8	6
Kwanobuhle	4	3
Total	20	15

The Uitenhage city planners allowed for secondary treated water supply to parts of the industrial sector of the town. A dam was constructed in the higher regions and an estimated 1Ml secondary treated sewage is pumped into this dam from where it gravitates back into the

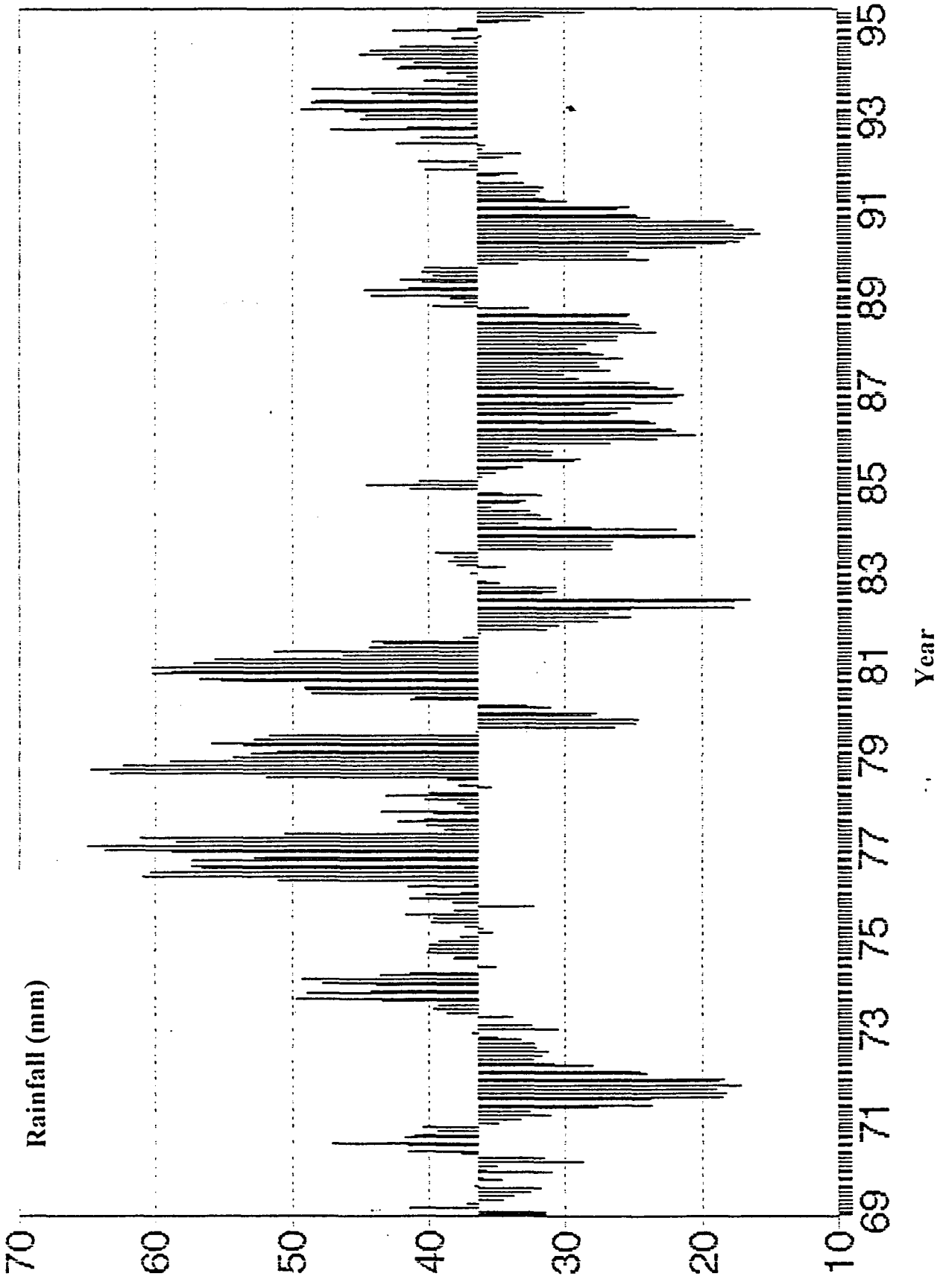

Figure 1: Rainfall statistics for Uitenhage over a 10-year period

industrial area. Uitenhage is therefore ideally suited to investigate the usefulness of membranes in this tertiary treatment role.

Table 4: Comparison of compositions of indigenous and imported water

23 January 1994	Groendal raw	Groendal final	Springs final	PEM
pH	5.89	7.8	4.84	7.13
TDS (mg/l)*	125	150	101	613
Conductivity (mS/m)	19	21	17	103
Colour (Pt C0 @ 455nm)	72	19	3	5
Turbidity (NTU)**	1.9	0.66	0.26	0.56
Total hardness***	21	38	20	260
Calcium (Ca^{++})***	8	27	7	104
Magnesium (Mg^{++})***	13	11	13	156
Total alkalinity***	6	15	4	214
Carbonate alkalinity***	0	0	0	0
Bicarbonate alkalinity***	6	15	4	214
Sodium (Na^{+})	23	23	19	154
Potassium (K^{+})	1.2	1.15	0.4	6.8
Iron (Fe^{+++})	0.41	0.06	0.02	0.09
Aluminium (Al^{+++})	0.07	0.41	0.07	0
Manganese (Mn^{++})	0.01	0.03	0.1	0
Chloride (Cl^{-})	39	41	36	135
Sulphate ($SO^{=}_{4}$)	0	16	0	108
Ammonia (NH_4)	0.19	0.07	0	0.04
Nitrate (NH_3)	0.3	0.4	0.5	0.5
Silica (SiO_2)	6.3	6.3	11.5	10.1
OA (mg/L)	6.8	4	0.2	12.6

*Total dissolved solids (TDS) **Nupheleometric turbidity units (NTU) *** as $CaCO_3$

However, although a large proportion of the industrial area is reticulated to receive this secondary treated sewage to reduce fresh-water intake by industry, the volume of reclaimed water currently used is not high. The quality of the reclaimed water is also not high and, as can be seen from Table 5, the water is essentially fit only for use in cooling and non-sensitive processing. It is reasonable to believe that the quality of the secondary treated water will deteriorate further during periods of drought because of intake of higher volumes of water from Port Elizabeth Municipality. The current permit from the Department of Water Affairs states that at least 80% of the water drawn from the Groendal dam must be discharged after treatment into the Swartkops River.

Table 5: Monthly average performance data of the Kelvin Jones Sewage Works

	*COD (mg/l)		**SS (mg/l)		***Cond (mS/cm)		NH_3		NO_3
Month	Raw	Fin	Raw	Fin	Raw	Fin	Raw	Fin	Fin
1992									
July	1369	68	516	16	261	219	46	2	3.1
Aug	1354	66	641	14	258	218	40	2	2.5
Sept	1212	65	461	14	228	189	38	2	1.3
Oct	1280	71	469	18	240	201	33	1	4
Nov	1118	59	567	14	254	216	29	0	6.7
Dec	986	61	424	8	208	174	35	0	4.6
1993									
January	1333	56	535	7	181	145	32	1	2.7
February	1271	57	546	5	173	140	33	1	2.8
March	867	60	372	5	174	138	33	1	2.7
April	974	65	494	14	217	172	21	2	4.3
May	1033	68	419	13	198	162	30	2	7.3
June	1134	70	493	14	209	170	44	2	5.1
July	1023	87	379	18	226	186	53	5	1.9
August	1133	63	456	10	217	170	54	4	0.5
September	1008	63	398	11	227	191	44	4	3.3
October	1095	60	458	14	268	230	44	4	2.5
November	1328	59	691	13	224	190	43	7	0.6
December	1411	67	865	13	255	209	43	5	0.9
1994									
January	1083	61	749	13	212	182	27	4	1.6
February	972	60	410	11	207	179	39	4	0.7
March	893	61	373	11	205	178	39	1	0.8
April	851	55	372	9	180	153	42	1	3.3
May	1171	64	493	11	217	180	46	1	3.1
June	1040	80	423	16	231	198	44	1	0.8
July	951	86	364	20	238	204	44	2	3.4
August	839	77	341	16	268	229	36	2	1.7
September	929	69	374	13	231	201	43	2	0.2
October	864	57	357	10	207	180	39	2	0.2
November	895	50	389	8	174	148	37	3	0
December	808	49	423	9	171	143	35	2	0.2

*Chemical oxygen demand (COD) **Suspended solids (SS) ***Conductivity (Cond)

If one considers that the water drawn from the Groendal dam is augmented from other sources, that is PEM and the Springs, a substantially greater proportion of water can be re-used than at present. However, the low quality of the secondary water is a deterrent.

2. MEMBRANE FILTRATION OPERATIONS

A. Ultrafiltration

Ultrafiltration is a pressure-driven membrane separations operation used to remove dissolved and suspended (particulate and colloidal) macromolecular species from water. Small pores in the skin layer of ultrafiltration membranes enable separation to be achieved by a sieving mechanism whereby dissolved or suspended species that are larger than the pores in the skin layer are retained while those that are smaller will pass through the membrane.

Ultrafiltration is capable of reducing the viral and bacterial counts in water to acceptable levels since the pores in these membranes range in diameter from 2 to 30nm, depending on the molecular-mass cut-off (MMCO) of the membrane. However, the sizes of pores in the membranes are not absolute since the sizes of the pores in the skin of the membrane vary. It is important therefore during the manufacture of these membranes that attention be given to control not only the average membrane pore sizes but to ensure narrow pore-size distributions.

The mechanism of retention of ultrafiltration membranes differs from that of sand-filtration in that the membrane is a surface filter and entrapment of retained species in the bulk of the membrane does not occur as with sand filters. For this reason there is no break-through of retained species as commonly occurs with depth filters.

By definition, ultrafiltration membranes cannot desalinate water. However, the membranes can reduce the concentration of hydrous species such as ferric and aluminium substantially. If a secondary layer of retained species build-up on the membrane surface (concentration polarization or gel-layer), the membranes can also reduce slightly the concentration of divalent species such as sulphate, magnesium and calcium.

B. Nanofiltration

Nanofiltration is an intermediate desalination operation. It is also referred to as a water softening operation as it retains divalent species to a far greater degree than it does monovalent species such as sodium and chlorides. The retention performance of these membrane is not based on size exclusion, but rather on the principle of solution diffusion,

that is, retention is based on the different rates of diffusion of the species through the membrane.

Nanofiltration membranes are capable of retaining organic species of very low molecular mass and as such the process is excellent for colour removal. The membranes are more dense than ultrafiltration membranes, so that they have greater capabilities for the removal of microorganisms.

However, the operating pressure of these membranes is an order of magnitude higher than that of ultrafiltration; typically from 1 to 1,5MPa.

III. MEMBRANE AND MODULE CONFIGURATIONS

1. SUPPORTED TUBULAR MEMBRANES

Tubular membranes have the advantage of an open-flow channel so that they offer the possibility of operation on less than clean water. Similarly these membranes offer the possibility of very high water recovery rates as they can tolerate a higher concentration of suspended solids in the feedwater.

Tubular membranes are available in diameters that range typically from 8 to 25mm. They are cast on the inside of a filter tube welded from a non-woven spun-bonded polyester or polypropylene fabric. The narrow-bore 8mm diameter membranes are self-supporting at lower operating pressures (typically 2 to 3 bar). Although these pressures are adequate for operation of an ultrafiltration process, they are much below the operating pressure for nanofiltration. For this reason the tubular nanofiltration membranes must be housed in perforated steel tubes, which act as a pressure support system. The membranes are normally housed in a tube-in-shell arrangement. In one design the membranes are sealed to the perforated stainless steel support tubes at either end with a rubber grommet, and 18 individual tubes in a module are manifolded into a series arrangement by means of a specially designed end-cap bolted onto the tubesheet.

Plastic disks are used in another less expensive tubular module design. The injection-moulded plastic disks have 19 holes that form tubular passages when the disks are lined up correctly. The membranes are inserted into these bodies which in turn are inserted into a metal shroud. In a module arrangement in which the tubular membranes are connected

in series, the tubesheets are formed by inserting plastic return bends into the open ends of the membranes, and encasing the end-assembly in epoxy.

2. UNSUPPORTED CAPILLARY MEMBRANES

Capillary membranes have advantages in addition to those offered by the tubular configuration. They are self-supporting because of their narrow diameters (typically 0.7 to 2.5mm), and they may be pressurized internally or externally. The internally skinned membranes are operated from the lumen side, that is, they are internally pressurized and filtrate permeates from the inside to the outside. However, they may also be operated in the reverse direction (i.e. outside to inside) without collapsing. This may be used to introduce a back-flush by which the membrane surface may be cleansed of foulant deposits either by reverse flow of product water.

The use of air as a backflush medium for ultrafiltration membranes depend on the MMCO of the membrane. Excessively high air pressures would be required to backflush membranes with small pores to achieve convective transport of air because of the capillary forces due to the high surface tension of the water filling the pores. However, with membranes of larger pore diameters, typically >50nm, air may be considered as a means for backflushing the membrane by convective air transport.

Capillary membranes must also be incorporated in a membrane-holding device or module, before they can be put to any practical use. Two axial-flow membrane module prototypes were used during the study. The modules were of tube-in-shell cartridge-type design which proved very simple to scale up to larger-sized units. It was important, however, that the cost per cartridge be kept as low as possible, without reducing the efficiency of either the process or the design.

The idea of a cartridge module originated at the time when modules were devised for incorporation in the cross-face flow manifolds then under development in another WRC-funded programme. The simplest and least expensive manifold for the cartridge type modules comprised a row of uPVC T-pieces with their straight ends solvent-welded together. The modules, which were fitted with two O-ring grooves on either end (Figure 2), were then simply push-fitted inside the side-branches of the T-pieces where the O-rings provided a seal against the inside of the side-branch to prevent process fluid leakage.

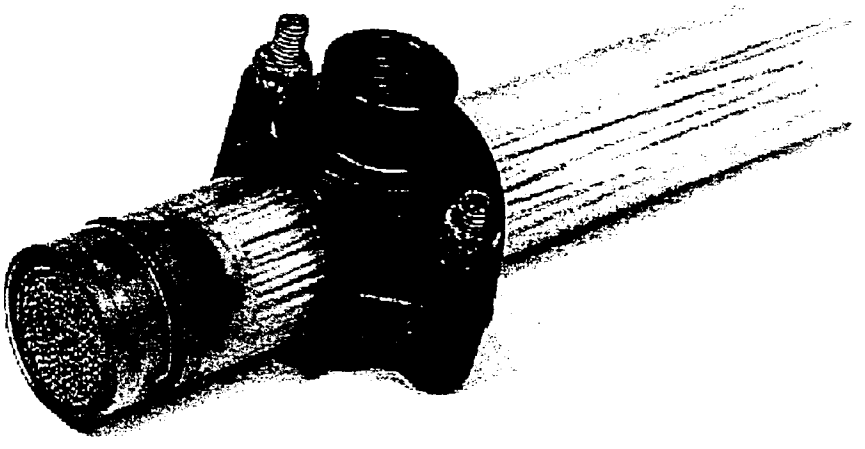

Figure 2: Photograph of a 40mm cartridge capillary membrane module

The across-face manifold (See Figure 3) was designed specifically to allow the feed-water to pass over the faces of the capillary membranes. The reason for this was not only for simplicity, but also to provide a means for counteracting the tendency for particulate material to accumulate at the module entrance, bridge, and eventually block the capillary lumen. As can be seen from the figure, the cartridge ends are placed in the manifold in such a way that the feed flow sweeps the faces of the cartridges. Because, under operating pressures the inlet and outlet manifolds would tend to move apart, the manifolds were braced so as to prevent this.

Across-face flow can be achieved by switching an inlet manifold recycle pump which circulates the process fluid in the manifold in a closed loop. This centrifugal pump can be operated continuously or be operated by means of a time switch.

In another embodiment of the cartridge-type design, the cartridges were fitted with removable flanges on either side. The modules could be fabricated from welded stainless steel tube, which is reasonably inexpensive, or uPVC tube. The photograph in Figure 4 shows the flanged-type module. Figure 5 shows that the stainless steel flange (which is an expensive part of the module) can be removed once the flange is slid backwards and the exposed steel circlip retainer ring (an O-ring may also be used) removed.

Both module designs were used in the experiments at Uitenhage. The module shown in Figure 3 was prepared from a 600mm-long transparent uPVC tube with an outside diameter of 40mm. A total of 119 membrane fibres with inside diameters of 1.07mm were packed into each of these modules. Each module had a membrane surface area of 0.2 m^2. O-ring grooves were machined into the tubesheet and four of the modules were mounted into the 40mm T-piece manifold of the UF test rig, giving a total membrane area of 0.8m^2.

The second flange-mounted module prototype had a surface area of 1m^2, housed within a 1,2m-long 50mm outer diameter stainless steel shroud. The membranes were internally skinned and a module contained 270 fibres with inside diameters of 1.2mm . The membranes had an instantaneous burst pressure of 2.3MPa. The modules were flange-connected.

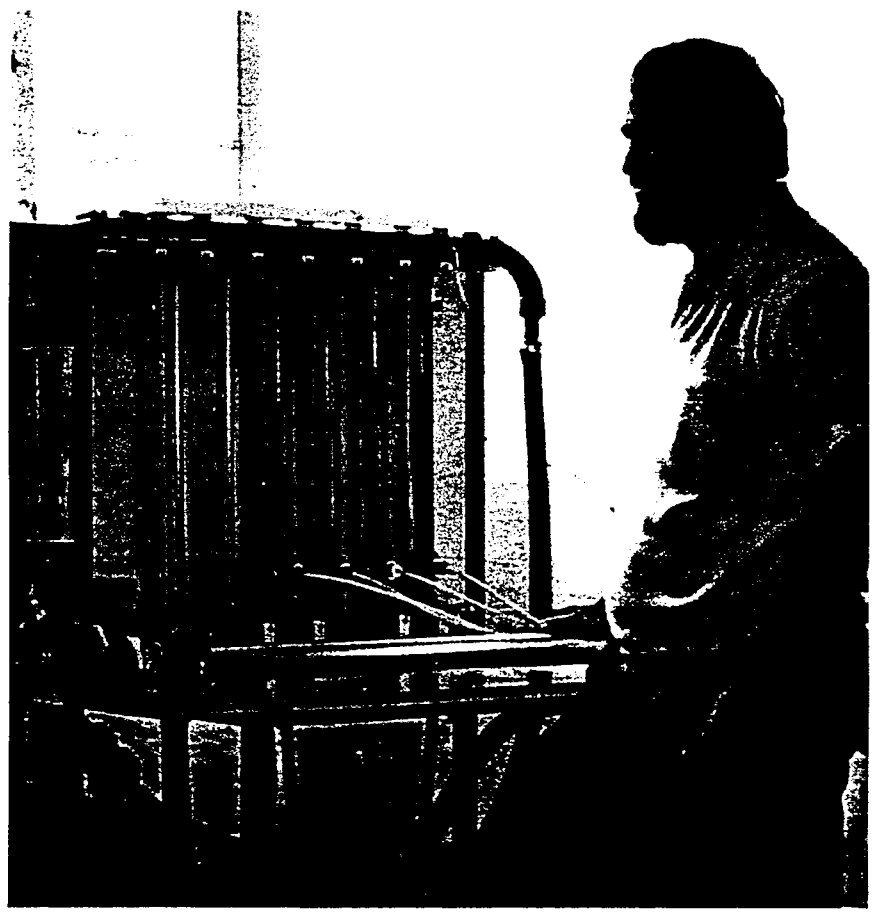

Figure 3: Across-face manifold for 40mm modules

Figure 4: Photograph of a 50mm axial-flow membrane cartridge with flanged connector design.

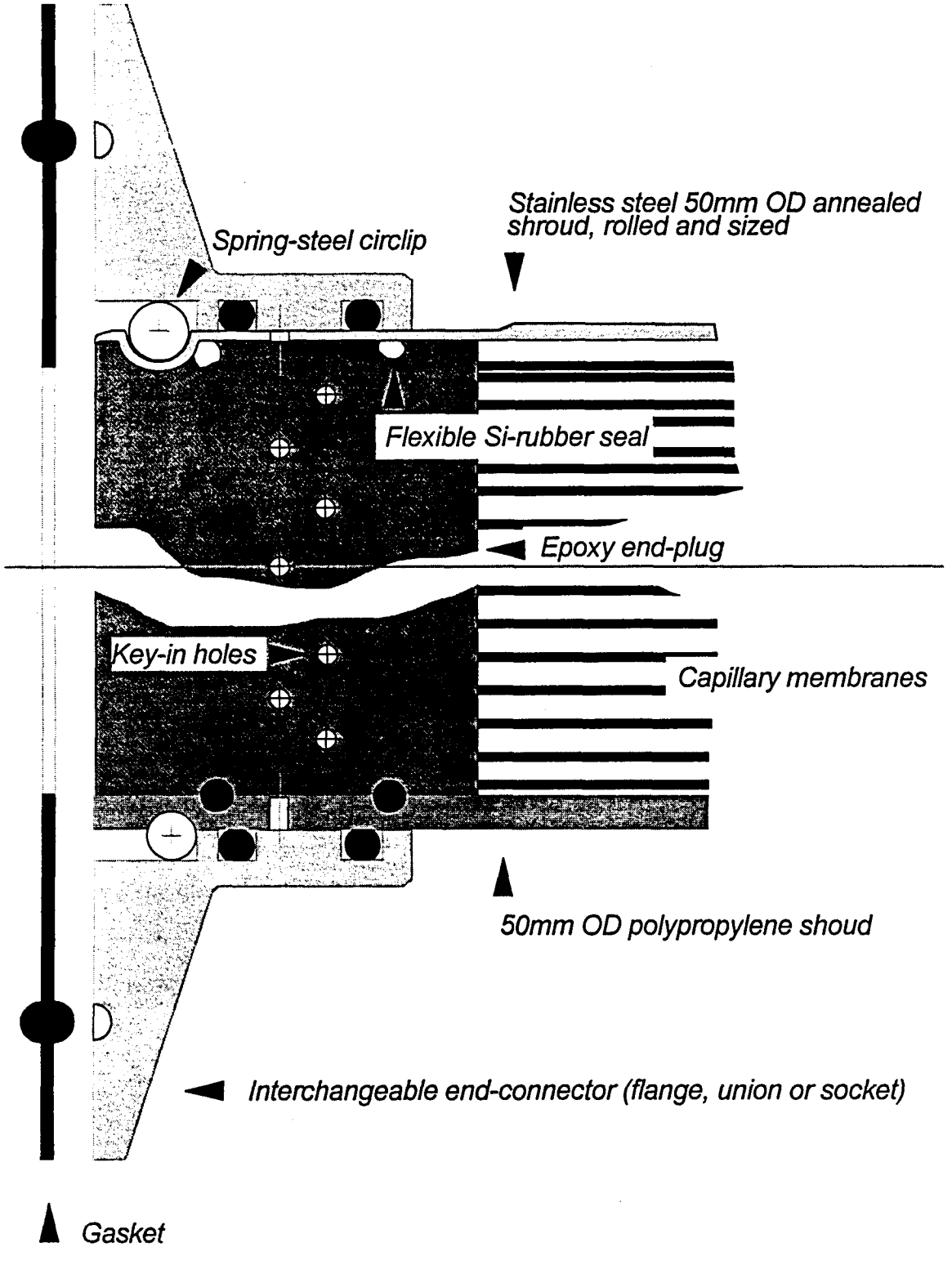

Figure 5: Schematic diagram of a 50mm flanged cartridge module

3. MEMBRANE PRODUCTION

A. Tubular nanofiltration membrane production

Pressure-driven membrane separation processes, as we know them today, owe their development to the discovery, early in the 1960s, of a technique for producing asymmetric reverse osmosis (RO) membrane films from cellulose acetate. The technique can also be used to produce non-desalting microfiltration membranes from poly(vinylidene fluoride) or poly(ether imide), ultrafiltration membranes from polysulphones or polyacrylates, or nanofiltration membranes from cellulose acetate. Nanofiltration membranes are loose, open RO membranes which, at medium to low operating pressures, discriminate in their separation of mono- and divalent inorganic species. These membranes also retain organic fractions that would otherwise pass freely through low-molecular-mass cut-off UF membranes. Nanofiltration is an economically and technically viable process for water-softening and/or removing colour from surface or process-effluent streams. In this section some aspects of the development of a low-operating-pressure tubular cellulose acetate nanofiltration membrane will be discussed.

(i) Phase inversion

Skinned (asymmetric) or unskinned (symmetric) membranes, are generally produced by phase inversion. In this process a homogeneous polymer solution is transformed into two liquid phases, one a polymer-rich phase and the other a solvent-rich or polymer-poor phase. The polymer-rich phase coagulates to form the membrane bulk, whereas the polymer-poor phase forms the matrix of interconnecting pores and passages within the skin and bulk structure of the membrane. Phase-inversion membranes can be formed from any polymer mixture which forms a homogeneous solution under certain conditions of composition and temperature, but which separates into two phases at other compositions and temperatures, provided that:

- ☐ the two phases that form during phase inversion are both continuous; and
- ☐ solvents, non-solvents and polymer additives that are used in formulations are soluble in the non-solvent medium used as coagulant.

In the wet-phase inversion process, water is the most commonly used coagulant for effecting this change in phase.

(ii) Membrane fabrication

Any factor that has an effect on the kinetics or thermodynamics of the inversion process will affect the morphology and the transport performance of the membrane. The following are some of the important factors that must be considered in the design of a membrane production protocol:

- ☐ nature of true solvents, latent and non-solvents used;
- ☐ polymer and inorganic additives used in the casting formulation;
- ☐ the membrane-forming polymer material(s);
- ☐ relative concentrations of the various components of the casting formulation; and
- ☐ viscosity and temperature of the membrane-forming dope.

Other factors include:

- ☐ temperatures of the extrudate, environment and the coagulant;
- ☐ air-gap, or time of membrane exposure between point of film extrusion and coagulation;
- ☐ inorganic and solvent additives and concentration-levels in the coagulation bath; and
- ☐ rate of membrane production.

(iii) 2-Level factorial experiments

A broad field of statistics is devoted to the planning of experiments. One of these experimental designs is the 2-level factorial experiment [1]. This experimental design involving n factors (i.e. the 2^n factorial), requires 2^n combinations of two levels for each of the n factors (i.e., 2^n experiments or treatment combinations in total). In a full factorial design, in effect, each of the n factors is considered at both a low level and a high level, and the variable considered is transformed to a minus for the low level or a plus for the high level (See the layout given in Table 6). These designs offer an ideal means by an experimental region can be explored to gain maximum information with the least amount of experimentation, and they have formed the basis of the approach to establish fabrication protocols by which a high-flux 40% NaCl-retention nanofiltration membrane can be produced.

(iv) Membrane formulation

A large number of variables need careful control during the fabrication of membranes to ensure replication and consistency in the performance of the membranes produced. On the other hand, by changing the level of factors such as the casting-solution formulation, membrane-annealing temperature and time, and even ambient conditions such as humidity and temperature etc., the performance of such a membrane-system can be adjusted to different values. However, membrane flux is an important economic consideration, and much effort is expended to increase membrane flux performance. Earlier work indicated that the retention performance of CA membranes can be closely controlled by adjusting the level of only four factors (only, however, if the levels of a number of other factors are kept constant). The factors that were considered in this study were:

- ❑ polymer concentration in the casting-solution formulation;
- ❑ acetone (solvent)-to-formamide (non-solvent) ratio in the formulation;
- ❑ concentration of a non-solvent modifier (here expressed as percentage of the solvent, acetone fraction in the formulation); and the
- ❑ membrane annealing temperature. The four-component formulation is completely described by the three factors that relate to the casting solution.

(v) Experimental approach to membrane development

The following experimental approach was used to determine the fabrication protocols for a productive 40% NaCl-retention nanofiltration membrane:

- ❑ explore the experimental region in the above four factors by means of two-level factorial experiment(s);
- ❑ model the flux and retention response by multiple linear regression to fit a generalized Taylor series model:

$$y^* = \beta^o + \sum_{i=1}^{n} \beta^i x_i + \sum_{j=i+1}^{n} \sum_{i=1}^{n} \beta^{ij} x_i x_j + \ldots$$

- ❑ conduct experiments at the centre-point of the factorial experiment to determine how well the real response surfaces are presented by the planar Taylor series model (The experimental design used did not provide the necessary degrees of freedom to include coefficients of higher order); and
- ❑ investigate the flux and retention regression equations numerically to obtain those fabrication conditions that will ensure the production of a membrane with

optimum flux at the specified NaCl retention of 40%.

(vi) Membrane evaluation

The membranes were evaluated against 2g/l NaCl in a closed-loop test system the temperature of which was controlled at 20±0,1°C. The operating pressure was maintained at 1MPa, the linear cross-flow velocity in the 13mm tubular membrane at 1m/s and the recovery was kept at zero percent. The membranes were contained in 500mm-long test cells. The performance of the membranes was judged by water-flux, expressed as litres per square metre membrane area per hour (Lmh), and percentage conductivity retention of the NaCl after 4h of operation. The performance of CA membranes can be compared by the log relationship of their pure-water permeability and salt permeability coefficients. The basic equations for transport through an RO membrane are:

water flux: $F_1 = A\left[\Delta P - \left(\pi_W - \pi_p\right)\right]$

and the salt flux: $F_2 = B\left[C_W - C_p\right]$

ΔP	pressure difference across the membrane
$\Delta\pi$	osmotic pressure difference across the membrane
ΔC	concentration difference across the membrane
A	pure-water permeability coefficient (A-value)
B	salt permeability coefficient (B-value)
π	osmotic pressure
C_W	NaCl concentration at upstream membrane interface
C_p	NaCl concentration at downstream membrane interface

As the desalinated water product permeates through the membrane there is an increase in solute concentration at the membrane-brine interface. The magnitude of this concentration increase or polarization at the membrane interface depends on the relative rate of convective flow towards the interface, diffusive flow away from the interface and linear rate of flow across the membrane. The relationships given earlier have been suitably modified to calculate the A-values and B-values of tubular cellulose acetate membranes subject to concentration polarization, and under conditions of turbulent flow. These relations were used in the calculation of permeability coefficients shown later [2,3].

(vii) Numerical optimization

Numerical optimization was achieved by means of a software package, Eureka, coded for use on a personal computer. This package is powerful enough to solve equations with four variables simultaneously and was able to converge to an answer within 3 min on a 386SX (20MHz) machine. The numerical optimization procedure followed was to maximize:
flux:: $f^f(x_1, x_2, x_3, x_4)$ subject to the inequality constraints:
retention: $f^r(x_1, x_2, x_3, x_4) \rangle 40$
and $-1 \leq x_i \leq +1, \ (i = 1...4)$

(viii) Results and discussion

Thermal treatment in hot water is a well-known procedure used to increase the salt retention by cellulose acetate membranes. However, the densification of the skin-structure caused by the annealing step has the reverse effect on the water transport rate of the membrane. Figure 6 clearly shows the effect that annealing temperature has on membrane flux and retention performance.

An important aspect of this study was to determine whether any net gain in flux performance could be achieved if porosity-modifying additives were used to offset the reduction in flux that resulted from annealing. For this purpose, very small quantities of the non-solvents water, glycerol and formic acid were added to the formulation. Table 6 shows the factor levels studied for the different cases as well as the results of the full 2^4 factorial experiment in which formic acid featured as a non-solvent additive to the solvent used, namely acetone.

The flux and retention responses obtained from the 2^4 factorial experiment where formic acid featured as additive were regressed as follows:

Flux: $F = 40{,}874 - 3{,}396x_1 - 5{,}071x_2 - 9{,}776x_3 - 9{,}577x_4 + 1{,}547x_1x_2 - 1{,}671x_1x_3 + 1{,}103x_1x_4 + 5{,}454x_2x_3 + 0{,}0996x_2x_4 + 0{,}658x_3x_4 + 0{,}397x_1x_2x_3 - 2{,}192x_1x_2x_4 + 3{,}093x_1x_3x_4 + 0{,}156x_2x_3x_4 - 1{,}727x_1x_2x_3x_4$

Retention: $R = 26{,}988 + 3{,}661x_1 + 1{,}573x_2 + 9{,}420x_3 + 4{,}134x_4 - 0{,}491x_1x_2 + 2{,}281x_1x_3 - 1{,}565x_1x_4 - 2{,}878x_2x_3 - 0{,}529x_2x_4 + 1{,}564x_3x_4 - 0{,}439x_1x_2x_3 + 2{,}250x_1x_2x_4 - 2{,}453x_1x_3x_4 - 1{,}176x_2x_3x_4 + 1{,}600x_1x_2x_3x_4$

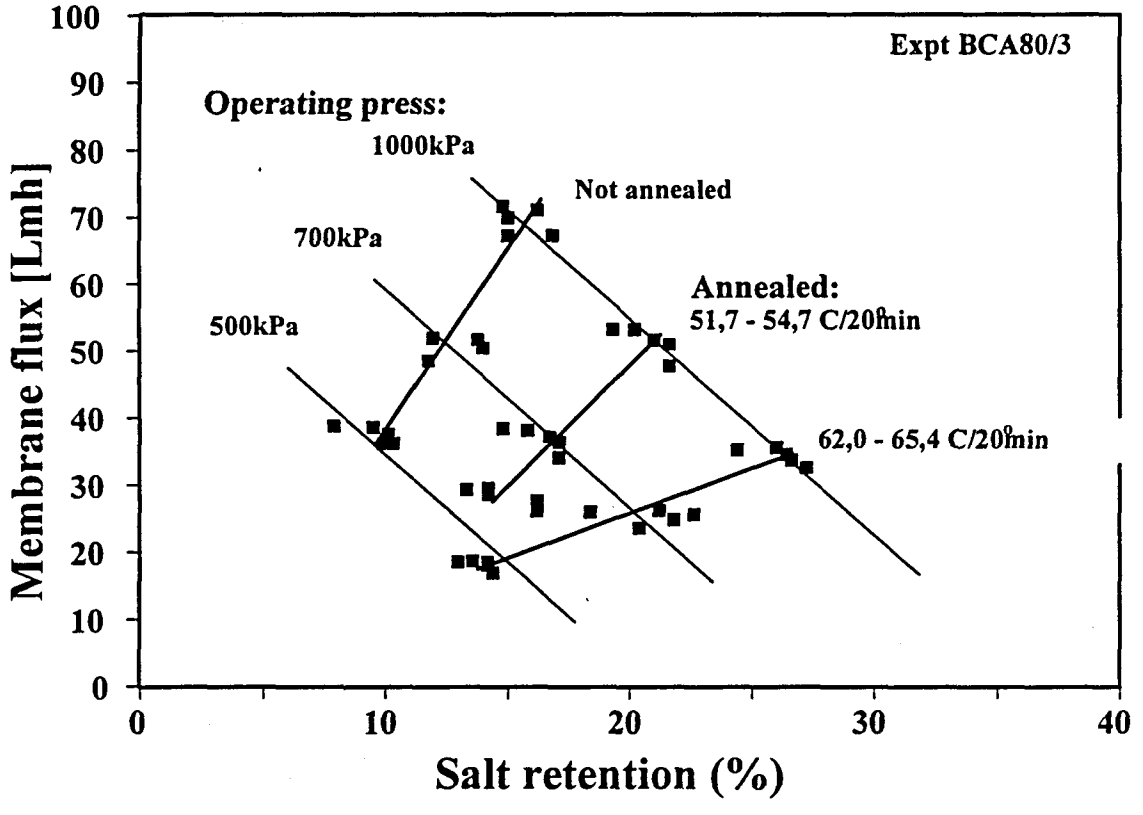

Figure 6: Flux and salt retention performance of CA membranes at different operating pressures and annealing temperatures

Table 6: Factor levels for 2^4 factorial and the flux and retention response for the treatment combinations of the full 2^4 factorial experiment

Factors		Variable level		
		Low	Centre	High
		-1	0	1
A	Cellulose acetate concentration (mm%)	23	23.45	23.9
B	Acetone/formamide mass ratio	1.4	1.45	1.5
C	Formic acid concentration in acetone (mm%)	0	0.75	1.5
D	Annealing temperature (°C)	75	78.5	82

Treatment	Variables				Flux	Retention
combinations	x_1	x_2	x_3	x_4	(Lmh)	(%)
I	-1	-1	-1	-1	73.6	10
a	1	-1	-1	-1	70.9	12.4
b	-1	1	-1	-1	47.6	19
ab	1	1	-1	-1	51.4	18.6
c	-1	-1	1	-1	44.1	26.9
ac	1	-1	1	-1	25.7	45.1
bc	-1	1	1	-1	42.7	25.9
abc	1	1	1	-1	35.9	36.3
d	-1	-1	-1	1	54.5	13.4
ad	1	-1	-1	1	45.7	16.7
bd	-1	1	-1	1	33.8	22.4
abd	1	1	-1	1	27.7	28.1
cd	-1	-1	1	1	19.5	46.1
acd	1	-1	1	1	21.8	44.1
bcd	-1	1	1	1	26.6	34.3
abcd	1	1	1	1	20.9	43.9

These regression equations illustrate the inverse relationship (opposite signs of the regression coefficients) between retention and flux, that is, an increase in salt retention is generally associated with a reduction in the permeate volume flow. With the assistance of the Eureka code, the equations were used to formulate numerically a 40% retention membrane with optimal flux performance. There was close correlation between predicted values and experimental results.

The pure-water-permeability and salt-permeability coefficients of membranes produced from formulations containing formic acid, glycerol and non-solvent modifiers are compared in Figure 7. From these, formic acid appears to be an attractive additive with a pronounced effect on salt retention. Regression lines drawn through the experimental and numerically generated membrane performances (Figure 8), give a clear indication that membrane performances can be further improved by formulating the membrane fabrication protocols numerically. Figure 9 shows the salt-retention performance of the formulated membrane within the experimental region demarcated in Table 6. Again there was close correlation between calculated values and experimental results.

(ix) Conclusions

2-Level factorial experiments offer a simple way to multiple linear regression because of the orthogonality of the experimental designs. When they are used in conjunction with numerical techniques, formulation of an intricate membrane system to achieve maximum flux performance for a given level of salt retention is simplified.

B. Ultrafiltration capillary membrane production

Capillary membranes are spun by extruding a membrane-forming solution through an annular (tube-within-tube) die (See Figure 10). This die contains an exit ring-opening for the casting solution and a centre opening for metering the core- or lumen-forming medium. When the wet-jet technique is used, a non-solvent coagulant is metered into the lumen of the nascent membrane. This fluid not only keeps the lumen from collapsing, but also participates in the coagulation process which leads to the eventual formation of the membrane. The outside of the membrane is also contacted with a non-solvent to enable the polymer to complete the membrane-formation process.

By adjusting the casting-solution formulation and coagulation protocols, membranes can be produced which:

- ❑ are internally or externally skinned,
- ❑ have dense, honeycomb or tear-shaped macrovoid substructure morphologies, and
- ❑ are ultrafilters or microfilters.

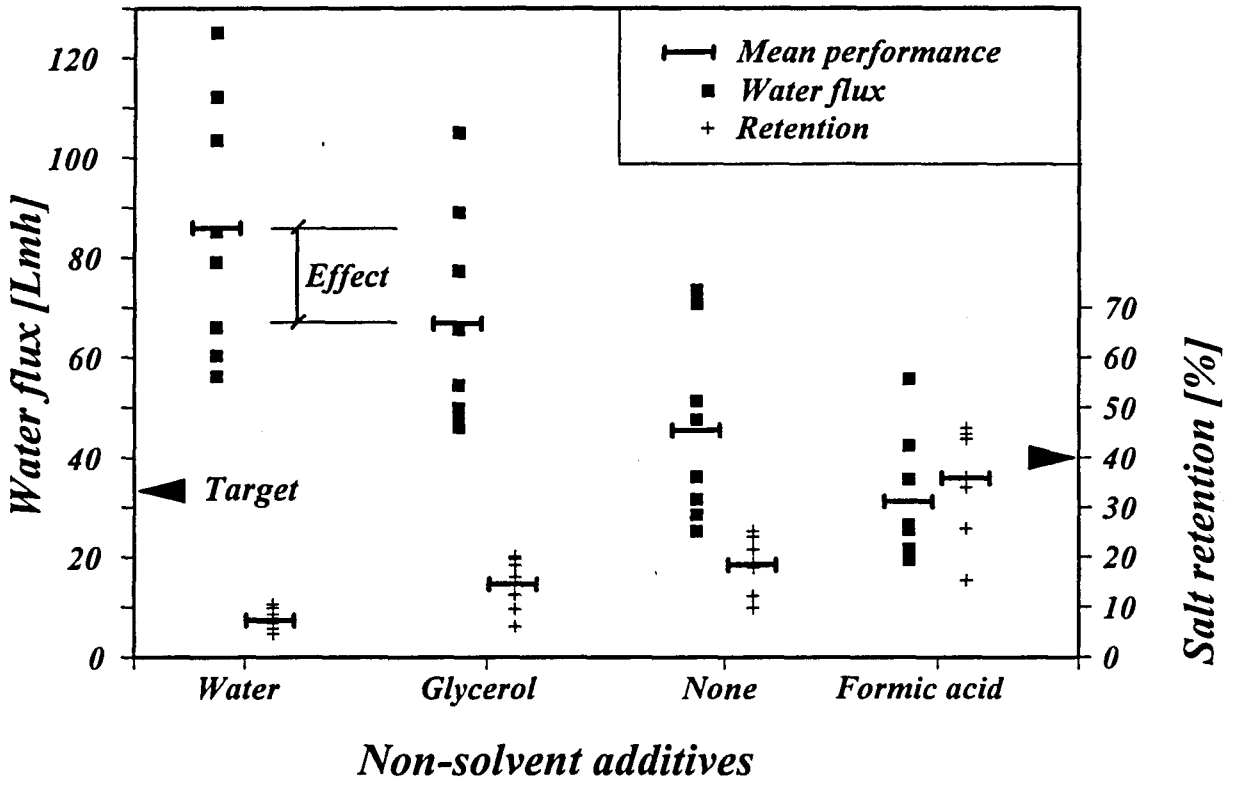

Figure 7: Effect of small quantity non-solvent additions on membrane performance

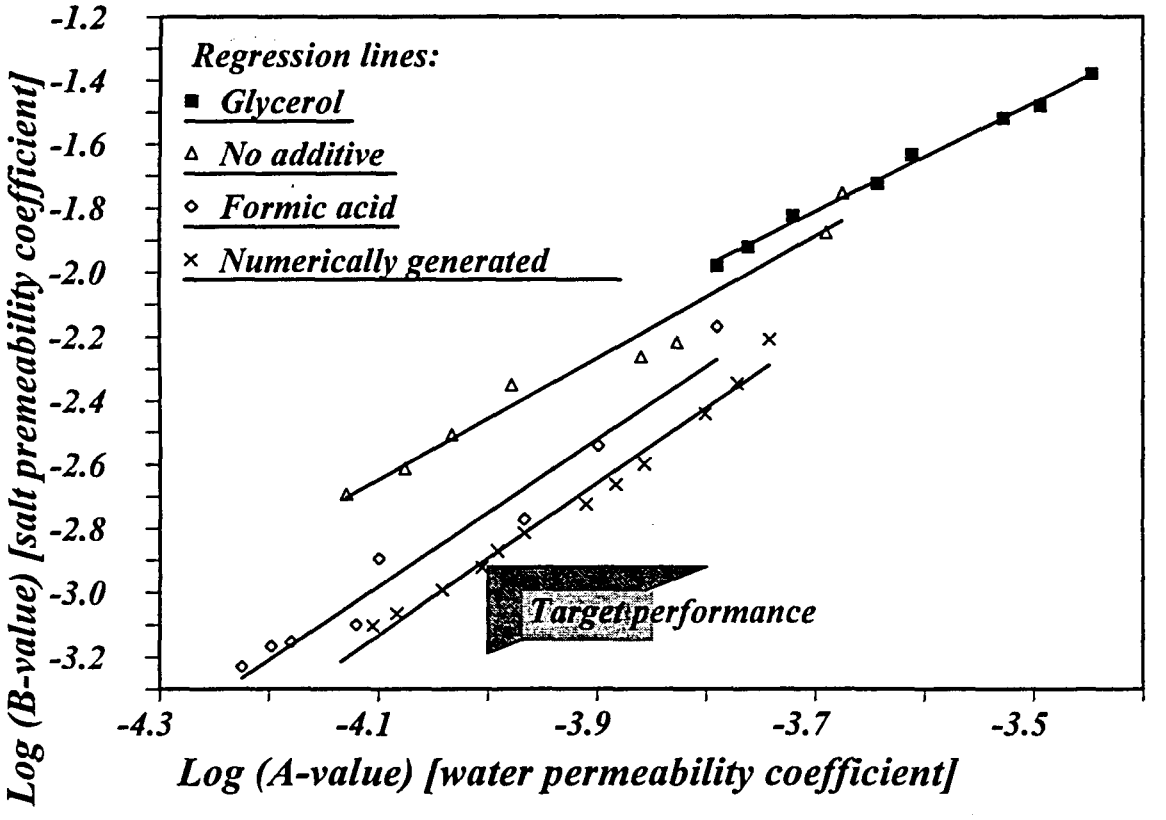

Figure 8: Comparison of membrane performance for various casting solution non-solvent additives

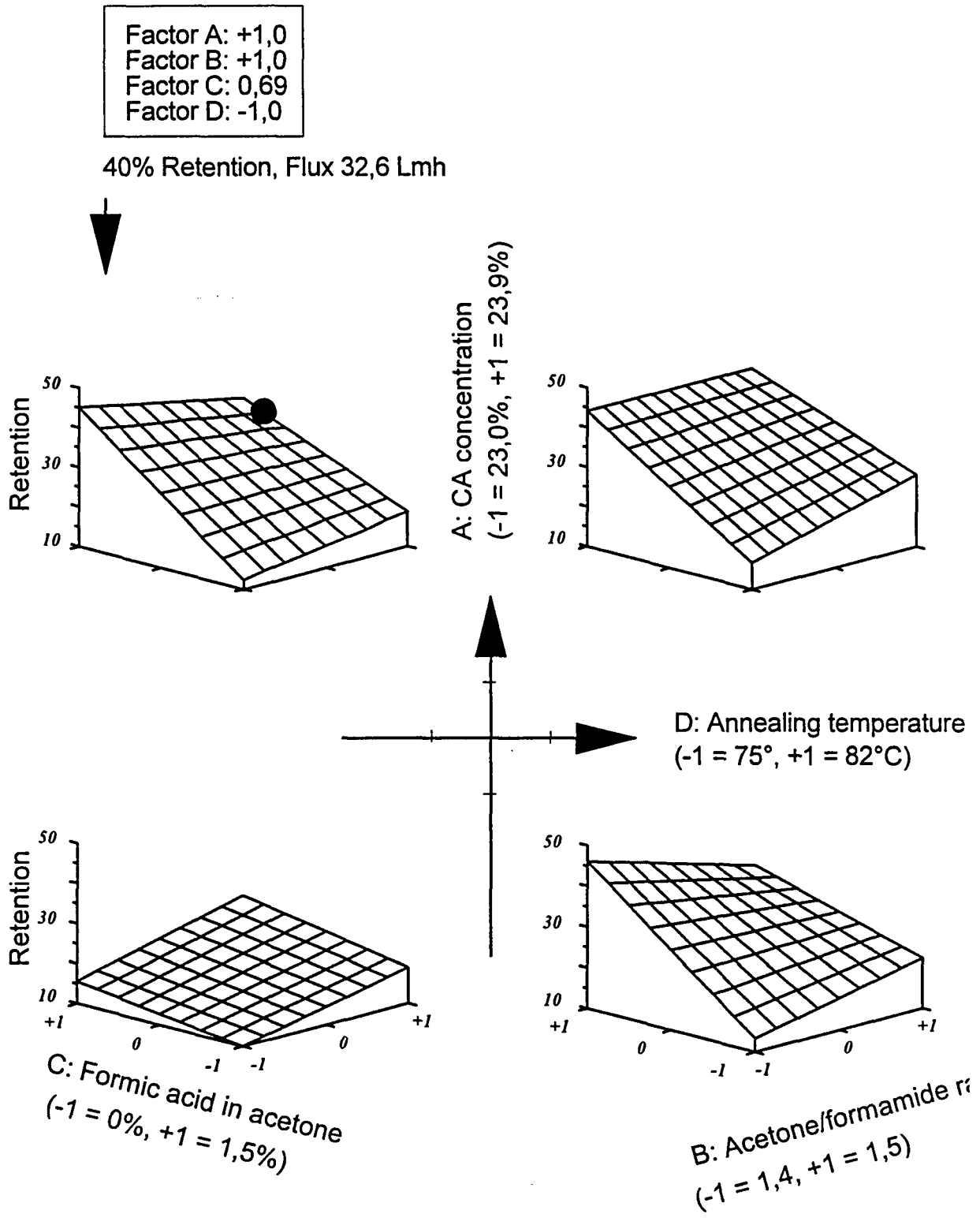

Figure 9: The retention response surface in the experimental window and retention performance of an optimum formulated membrane

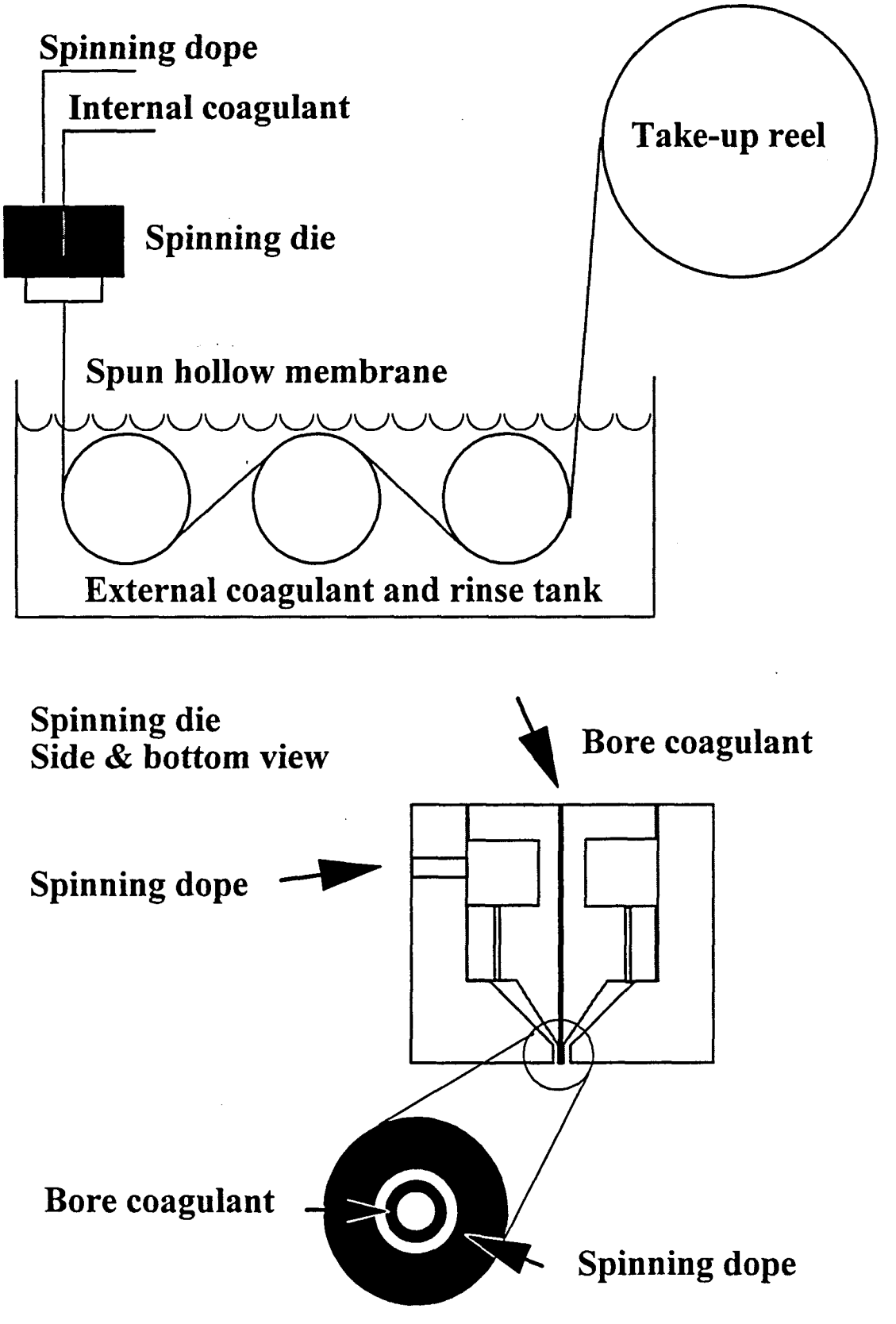

Figure 10: Annular spinning die for capillary membranes

If the membrane is cast into a strong non-solvent, the membrane will have a noticeable skin on the outside. If a membrane is cast into a weak non-solvent or a weak solvent, an imperfect external skin results. Likewise the core-fluid can be of similar composition, in which case a skin may or may not result on the inside.

The extruded membrane is drawn mechanically away from the spinneret. If a weak non-solvent or weak non-solvent mixture is used as the core coagulant, the viscosity of the internal wall remains relatively low and the membrane can be drawn to sizes a magnitude smaller than that extruded. However, if a strong non-solvent is used as core coagulant, the skin reaches maximum viscosity almost immediately and drawing at this stage will have relatively little effect on the membrane diameter.

Figure 11 shows the cross-section of a capillary membrane. The membranes are internally skinned, but have an outside skin of very low definition. When the definition of the external skin-layer is reduced the overall membrane resistance is reduced and the specific flux properties of the membrane are increased.

Code 748 capillary membranes, shown in Figure 11, was used in the Uitenhage experiment. These membranes were cast from a 26% (by mass) solution of poly(ether sulphone) in N-methyl, 2-pyrrolidone (NMP) solution. Additives were used in the formulation to modify the hydrophilicity of the membrane. Pure water at 22°C was used as internal coagulant, whereas an 20% (by mass) aqueous solution of NMP was used as external coagulant.

IV. MEMBRANE PROCESS OPERATION

1. NANOFILTRATION

A. System design

Figure 12 shows the layout of the experimental tubular-membrane-treatment plant. The level of the water in the feed tank was controlled by a ball valve and the system was operated on a feed-and-bleed basis. The recovery ratios were kept low because of the small membrane area and problems with temperature control. A triplex diaphragm pump was initially used as feed pump, but this was replaced after 3000h with a ceramic triplex piston pump. The system was further equipped with pressure gauges, rotameter and pressure control and by-pass control valves.

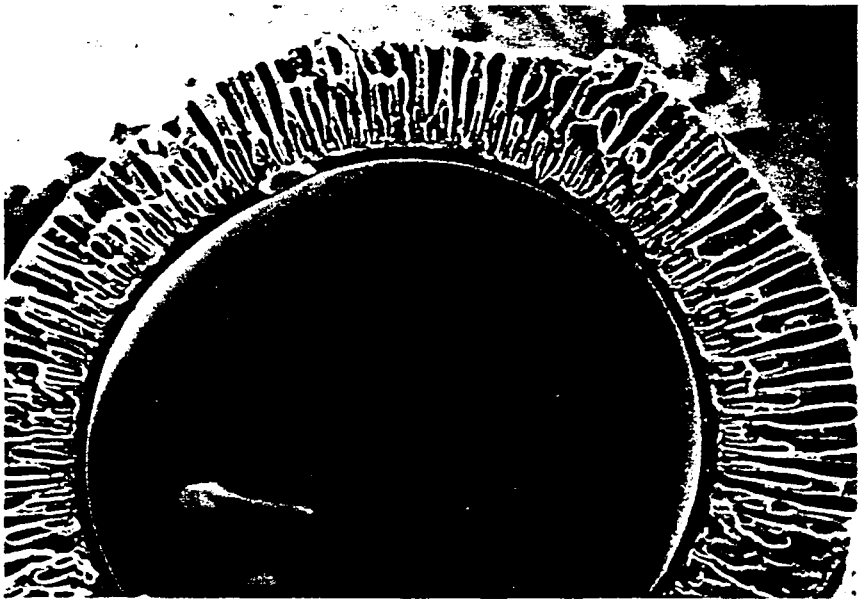

Figure 11: Micrograph of the cross-section of an ultrafiltration capillary membrane

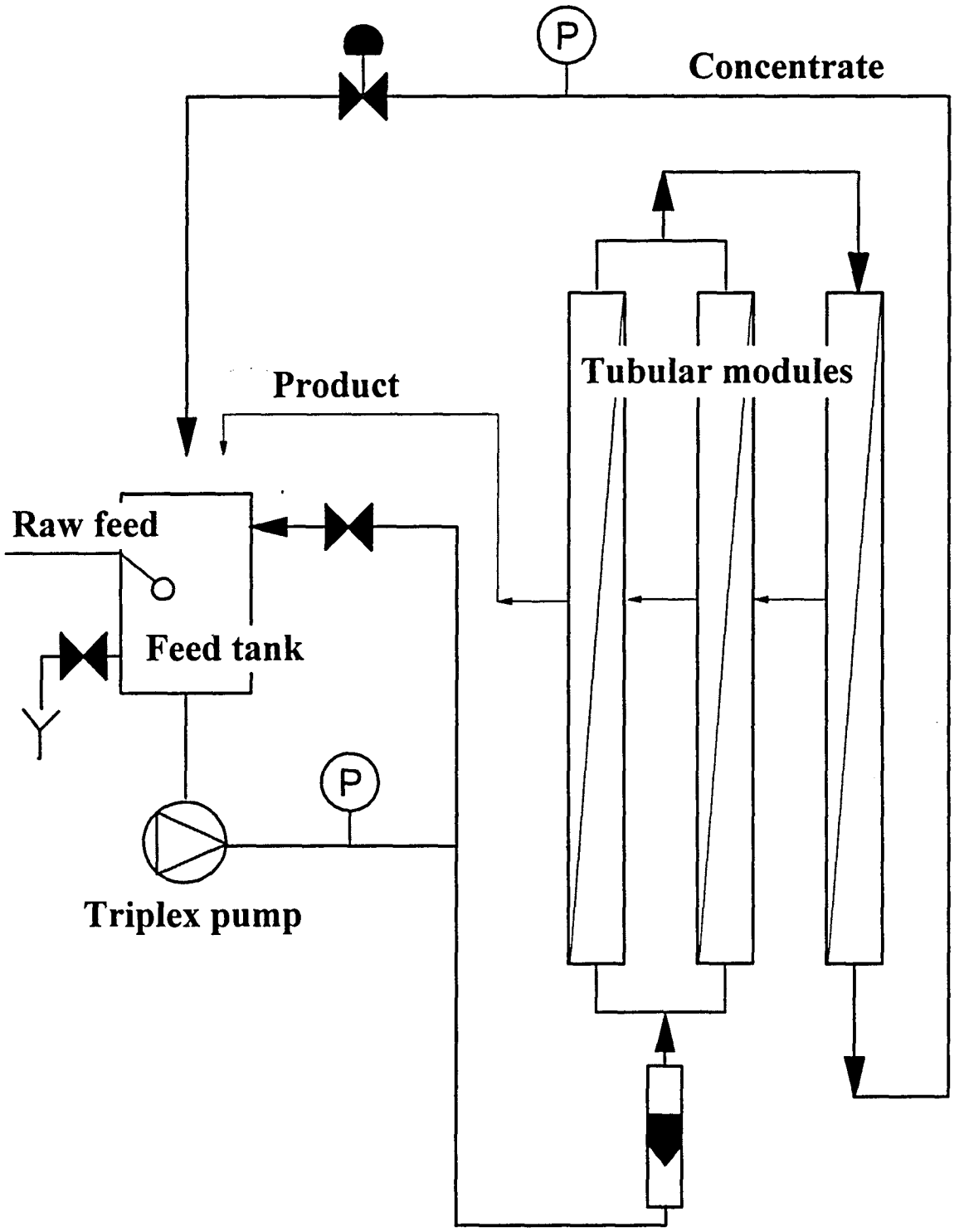

Figure 12: Layout of the nanofiltration system

The system was initially operated with a single module, but two additional modules were later added. The modules were operated in a 2 - 1 cascade, that is, the velocity in the second module was double that of the first two modules.

B. Membrane flux

The nanofiltration plant was operated for a period of more than 14 000h, initially with only one module, at an operating pressure of 1 000kPa. At 9 660h the membranes were replaced and a third module was installed. The flow arrangement was altered to a 2:1 cascade. The system was initially operated at inlet velocities of about 2,5m/s. This was later reduced to 1,5 and 1m/s respectively. Figure 13 shows the linear inlet velocity to the nanofiltration membrane rack (the operating times on all the graphs correspond).

The temperature of the feed water was not controlled and varied considerably during the period of operation, with temperatures below 16°C being observed during the winter months of July, and above 28°C during the summer months of November and December (see Figure 14).

The feed water to the tubular nanofiltration plant was not pretreated in any way and the water was accepted into the plant as such. No chemicals (oxidants or acid) were added to the raw incoming water from the maturation dam to correct the pH, which was, on average, greater than 7 pH units, or to disinfect the water. Operating at such pH levels, however, is not recommended practice for cellulose acetate membranes, but it was the intention to determine the life expectancy of the membranes operating at higher than recommended pH-levels.

The fact that the feed water was not chlorinated was in line with the argument that chlorination encourages aftergrowth: stimulation of microbial activity which metabolizes modified chemical species.

Figure 15 shows the combined flux performance of the membrane plant over the period of operation (the flux values shown were corrected for temperature). The flux values remained fairly stable over the period, declining towards the end when the 2:1 cascade was introduced and the inlet linear velocity was introduced.

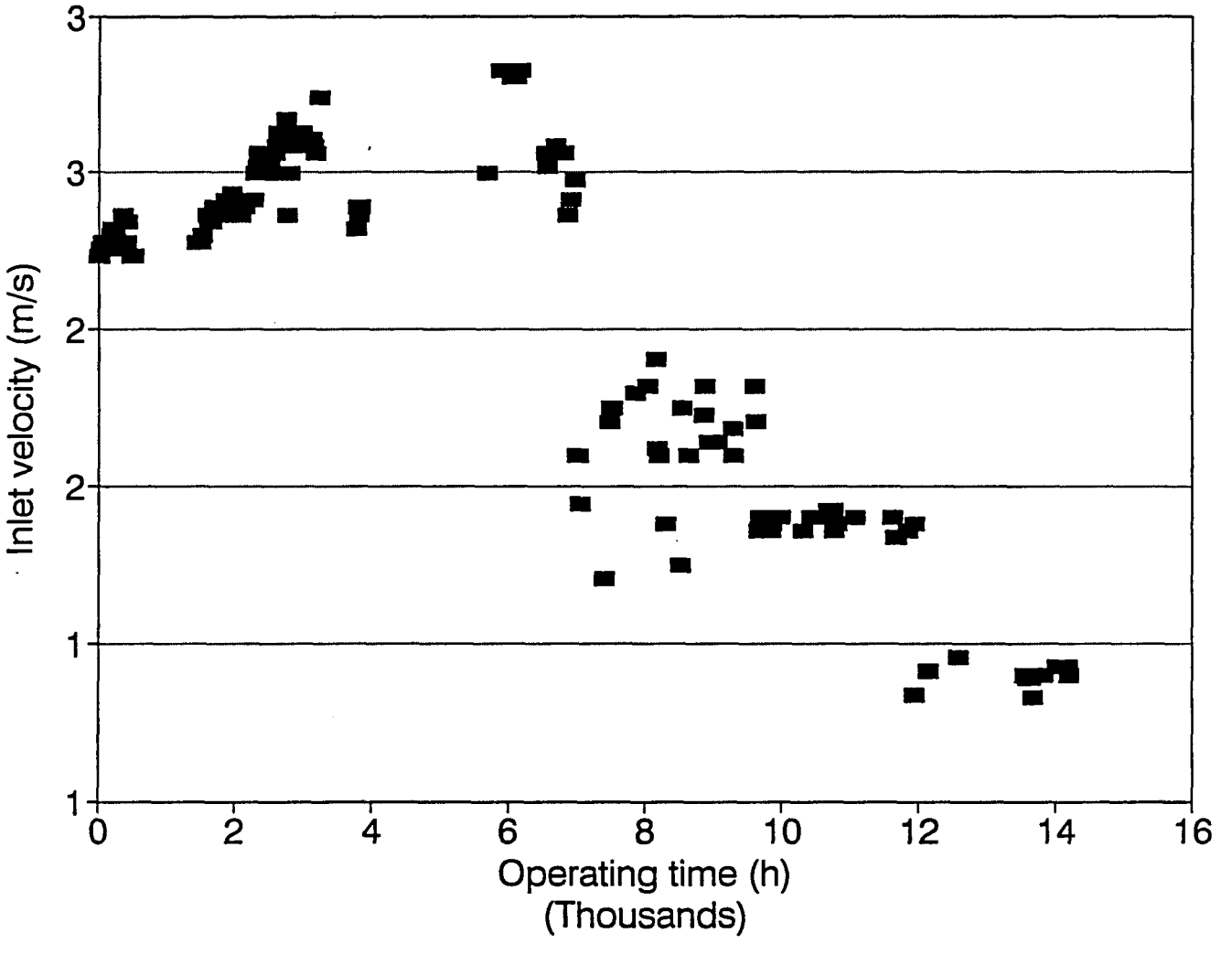

Figure 13: Linear inlet velocity to tubular nanofiltration membranes

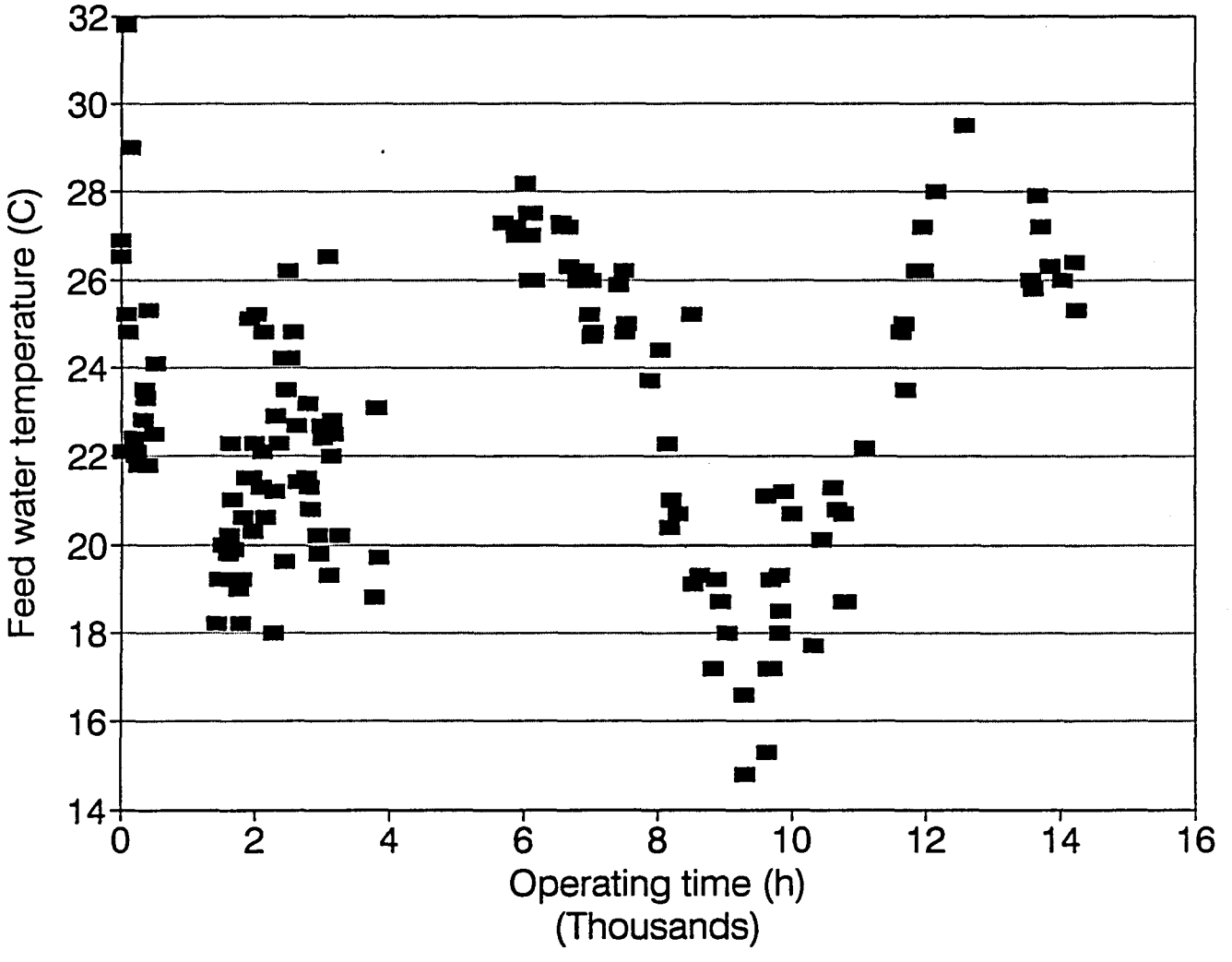

Figure 14: Temperature of raw water feed to tubular nanofiltration membranes

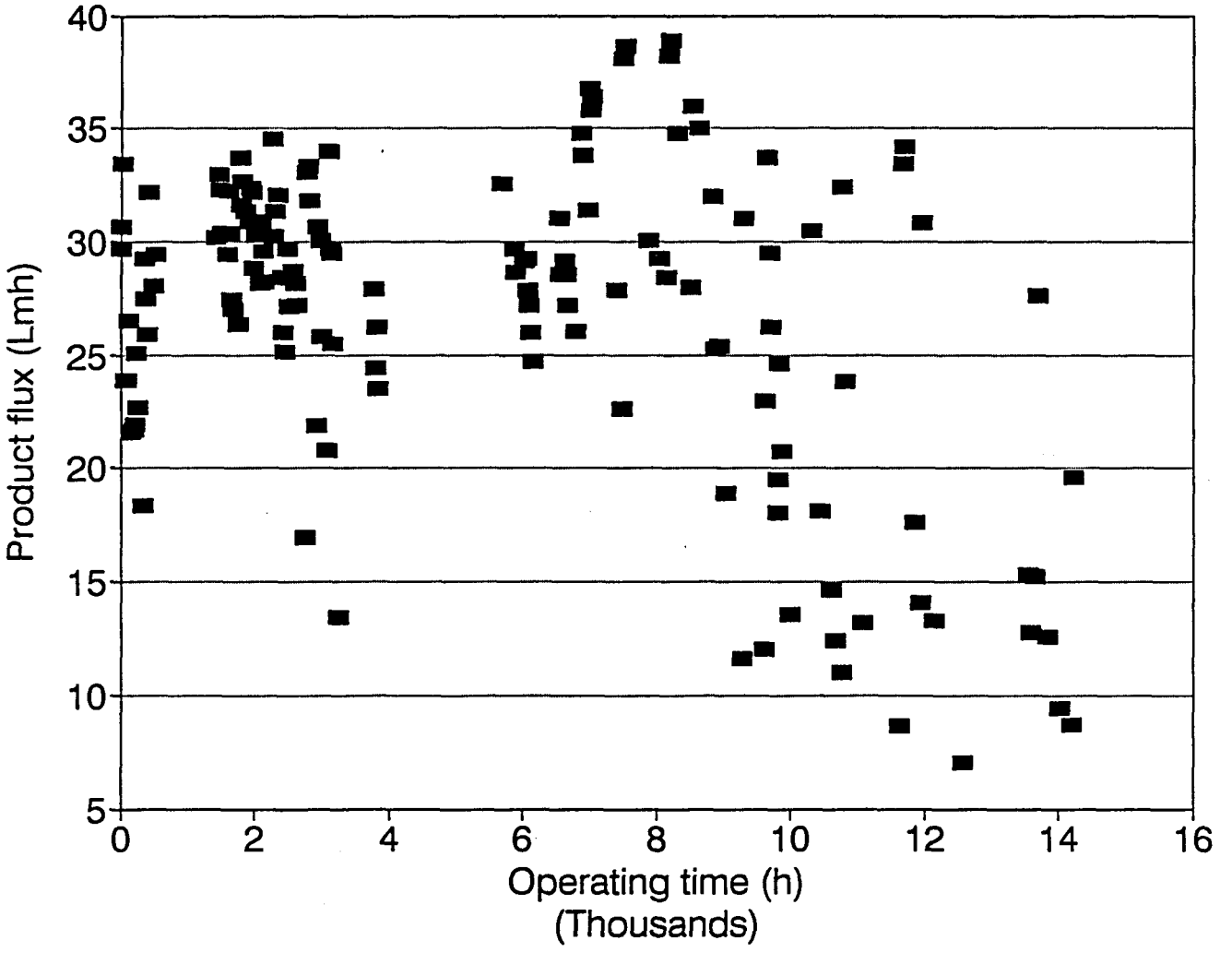

Figure 15: Product flux of tubular nanofiltration membranes

C. Colour removal

The colour-removal performance of the nanofiltration membranes was very high. The colour was measured spectrophotometrically at 455nm (Pt Co). Except for a period between 6 000 and 8 000h operating time when the colour component in the raw water was very low, and the retention capability of the membranes declined, a consistently high retention of colour was attained: on average above 96%. The colour of the product stream was continuously below 10 colour units.

Figures 16 illustrates how the colour content of the maturation pond effluent varied over the period of operation, and Figure 17 shows the colour content of the nanofiltered product water and thus the extent to which the nanofiltration membranes were performing (Figure 18). It must be noted that the sewage-treatment plant treats both domestic and industrial water, and that some of the industries, notably the textile industry, produce a highly coloured effluent. These results underscore the high potential of the nanofiltration process to reduce the organic load in water.

D. COD reduction

The capability of the cellulose acetate nanofiltration membranes to reduce the COD load of the maturation pond effluent is ilustrated in Figure 19. The membranes were consistent in their performance and continuously achieved retentions greater than 70% COD.

These results support the data shown in the earlier graphs and the ability of the nanofiltration membranes to polish water to a very high degree of acceptance.

E. Conductivity reduction

The nanofiltration membranes that were developed were designed to have low NaCl retention. The membranes that were used in the experiments, typically gave NaCl retention values of 30% in the laboratory, with an accompanied laboratory flux of 40LMH (1g/L NaCl feed, 20°C at 1MPa operating pressure).

The conductivity-reduction performance of the membranes was not very high, being on average above 45% (Figure 20). The membranes also showed signs of declining salt retention performance, which could be ascribed to fouling, and also possibly hydrolysis of the

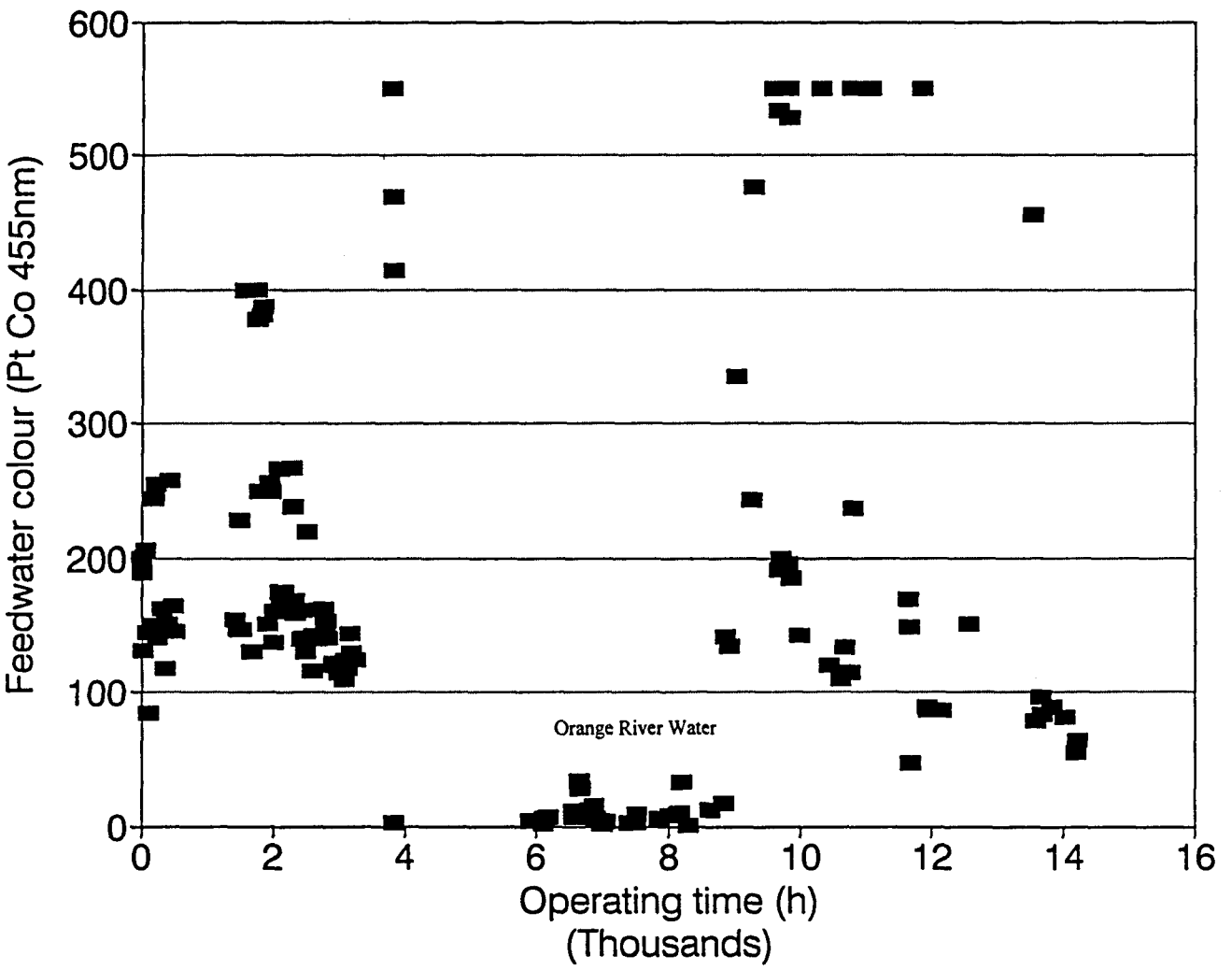

Figure 16: Colour content of maturation pond effluent feed to tubular nanofiltration membranes

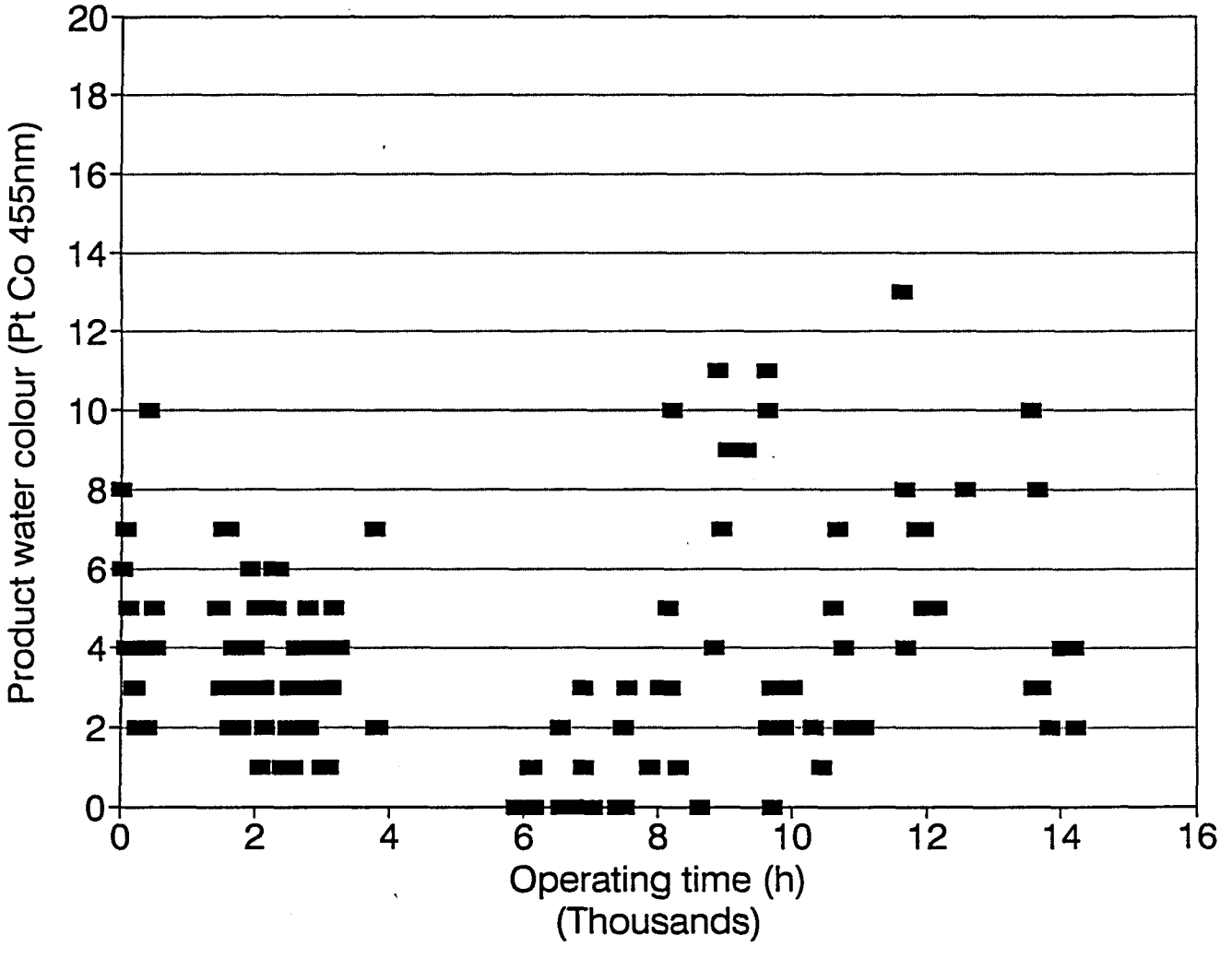

Figure 17: Colour content of nanofiltered product

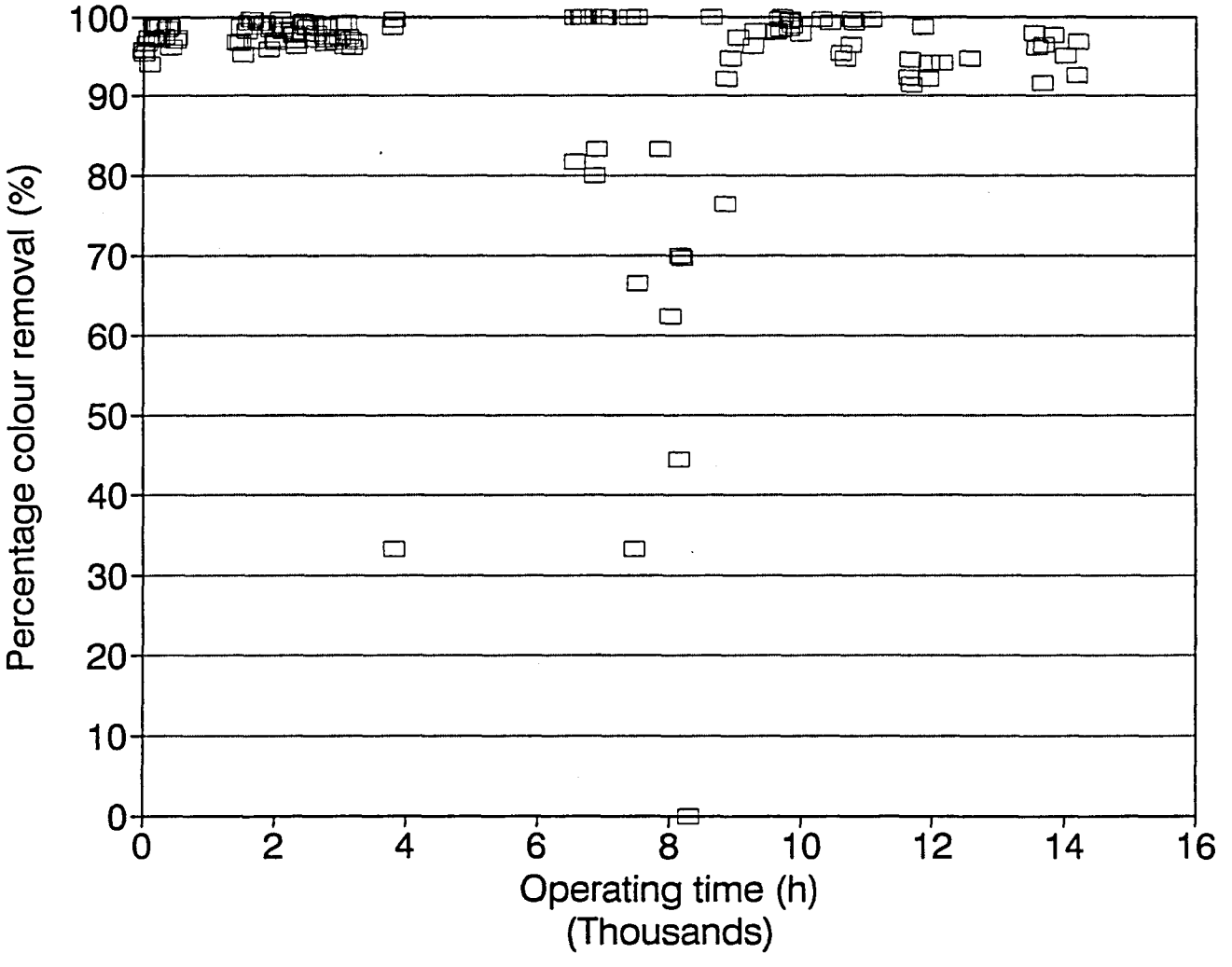

Figure 18: Percentage colour component removal by nanofiltration membranes

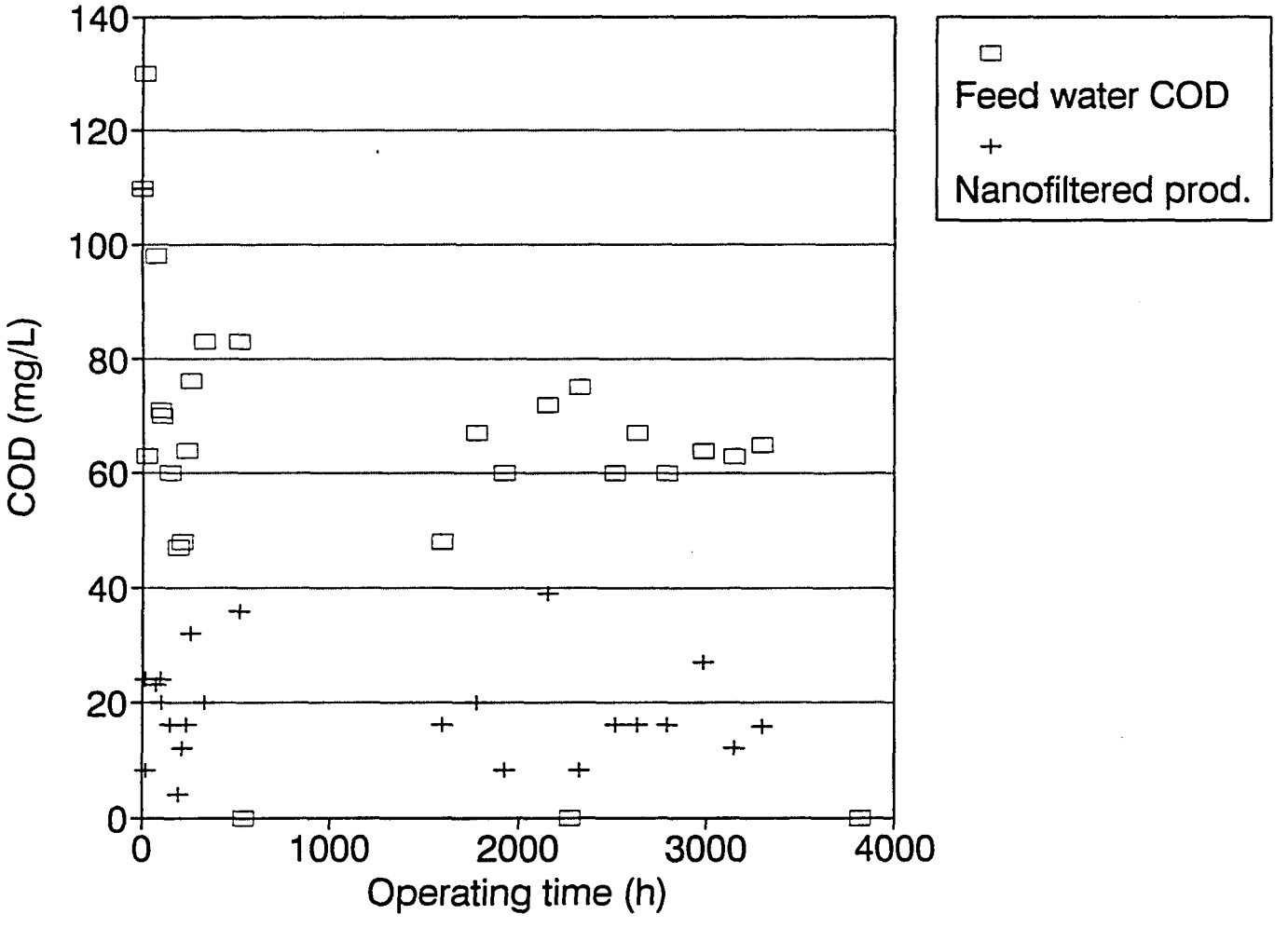

Figure 19: COD load in maturation pond effluent and nanofiltered product

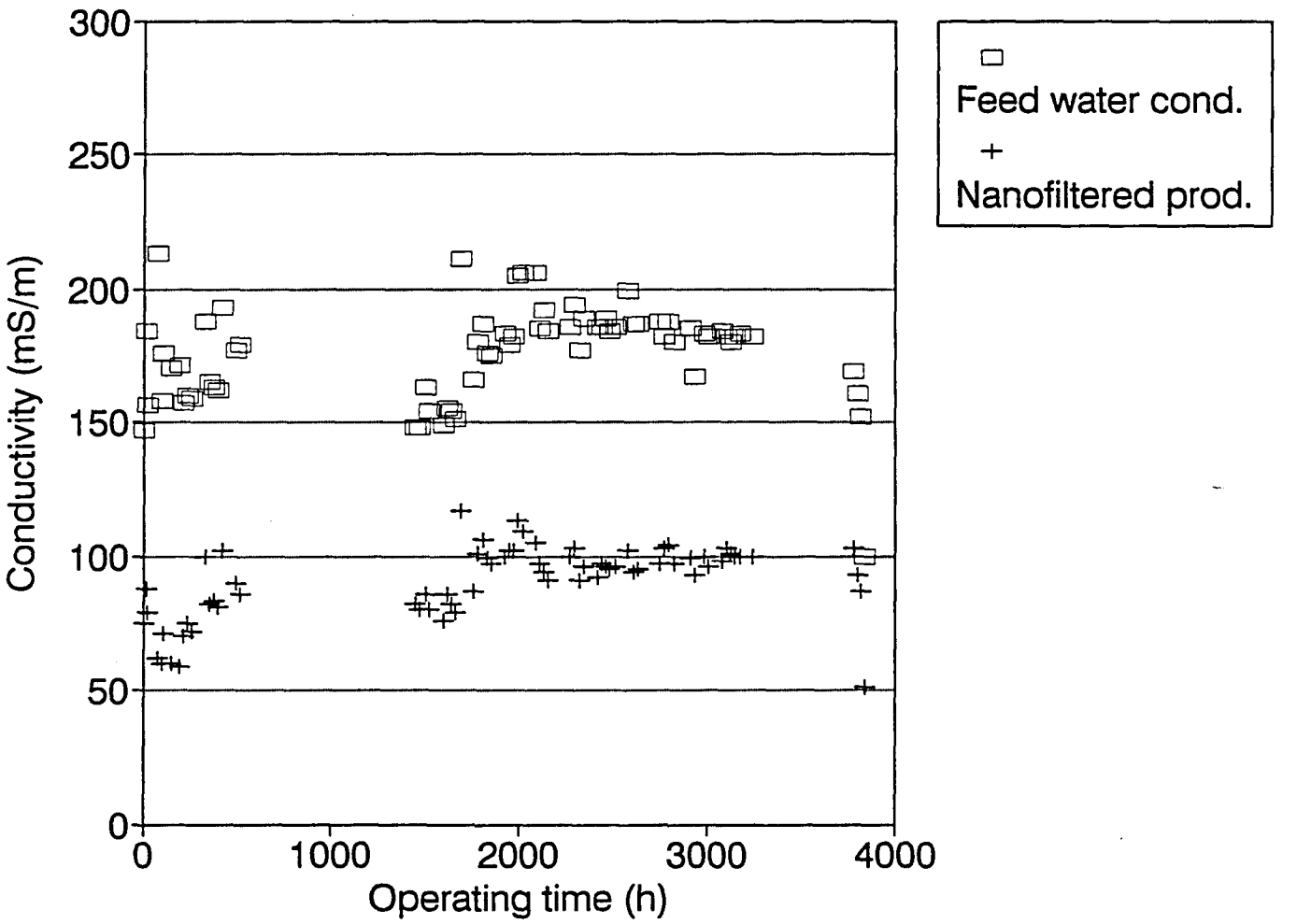

Figure 20: Conductivity of maturation pond effluent and nanofiltered product

cellulose acetate; no acid was added to the incoming water to reduce the pH level to more acceptable values for cellulose acetate membranes.

Salt retention of a fouled membrane was low, but after cleaning the salt retention improved as the flux improved.

The conductivity retention of a fouled membrane was low. However, cleaning restored both the flux and salt retention performance of the membranes.

F. Cleaning regimes

A range of cleaning regimes was used to maintain membrane flux performance. Different detergent flushes and foam ball swabbing were introduced from time to time; a list of the regimes used is shown in Table 7. Organic fouling seemed to be the likely cause of flux deterioration. The LSD64, a product of Lever Bros. showed promise as an alternative detergent for the removal of organic foulants (See Part VI of this report).

Air scouring was also introduced from time to time to loosen colloidal material deposited on the surface of the membranes. The system was pressurized by means of a positive displacement pump and this allowed air to be introduced into the system by venting the suction side of the feed pump.

Table 7: Detergent and other cleaning regimes for nanofiltration membranes

Cleaning regime	Duration
Water flush + 100mg/L NaMetabisulfite	10min
Glint (15%) 5mg/L; pH 7.5	30min
Punch 2%; pH 11	60min
Air scouring	5min intervals; 20min
Punch 2%; pH 11	120min
Biotex 1%	60min
LSD64 1%	120min
SCL 1% flush; Lever *LSD64* 1%	120min

2. ULTRAFILTRATION

A. System design

The capillary membrane test rig was of very simple design and consisted essentially of a feed tank and centrifugal feed and recirculation pumps (Figure 21). A 150μm vortex strainer was installed on the suction side of the feed pump to protect the pump and membranes from blockage by suspended material. The system operating-pressure was controlled by means of a pressure control valve and pressure gauges were used to measure the inlet and outlet pressures. Four 40mm cartridge modules (0,2m^2 membrane area each) were operated during phase I of the programme. The filtration capacity of the plant was increased during phase II of the programme when a 50mm flange-type module (1,0m^2 membrane area) was coupled to the outlet manifold of the four cartridge modules.

The membranes had instantaneous burst pressures exceeding 2MPa, and the system was initially operated at an inlet pressure of 200kPa. The modules were operated at an inlet-to-outlet pressure differential of 50kPa. When the 50mm module was installed, the inlet pressure to the bank of 40mm modules was 250kPa, so as to operate the 50mm module at an inlet pressure of 200kPa. The feed flow volume was maintained at 3 500L/h.

The membranes were operated under constant feed pressure, as opposed to constant flux.

B. Membrane flux

The process flux of the 40mm modules showed a severe and permanent deviation from the pure water flux measured in the laboratory after manufacture (Figure 22 and 23). During the initial stages of the programme the flux was routinely recovered by introducing rigid cleaning protocols. However, after 6 000h of operation, the cleaning procedures followed had a less pronounced effect on flux restoration and the flux eventually stabilized at 20Lmh. Figure 24 shows the typical saw-tooth response that the effective cleaning protocol had on membrane flux during the first 3 000h of operation.

No correlation was found between the flux of the cellulose acetate nanofiltration and polyethersuphone ultrafiltration membranes over the duration of the experiment. This could, in part, be due to the material of membrane construction, cellulose acetate being the more hydrophilic material of the two.

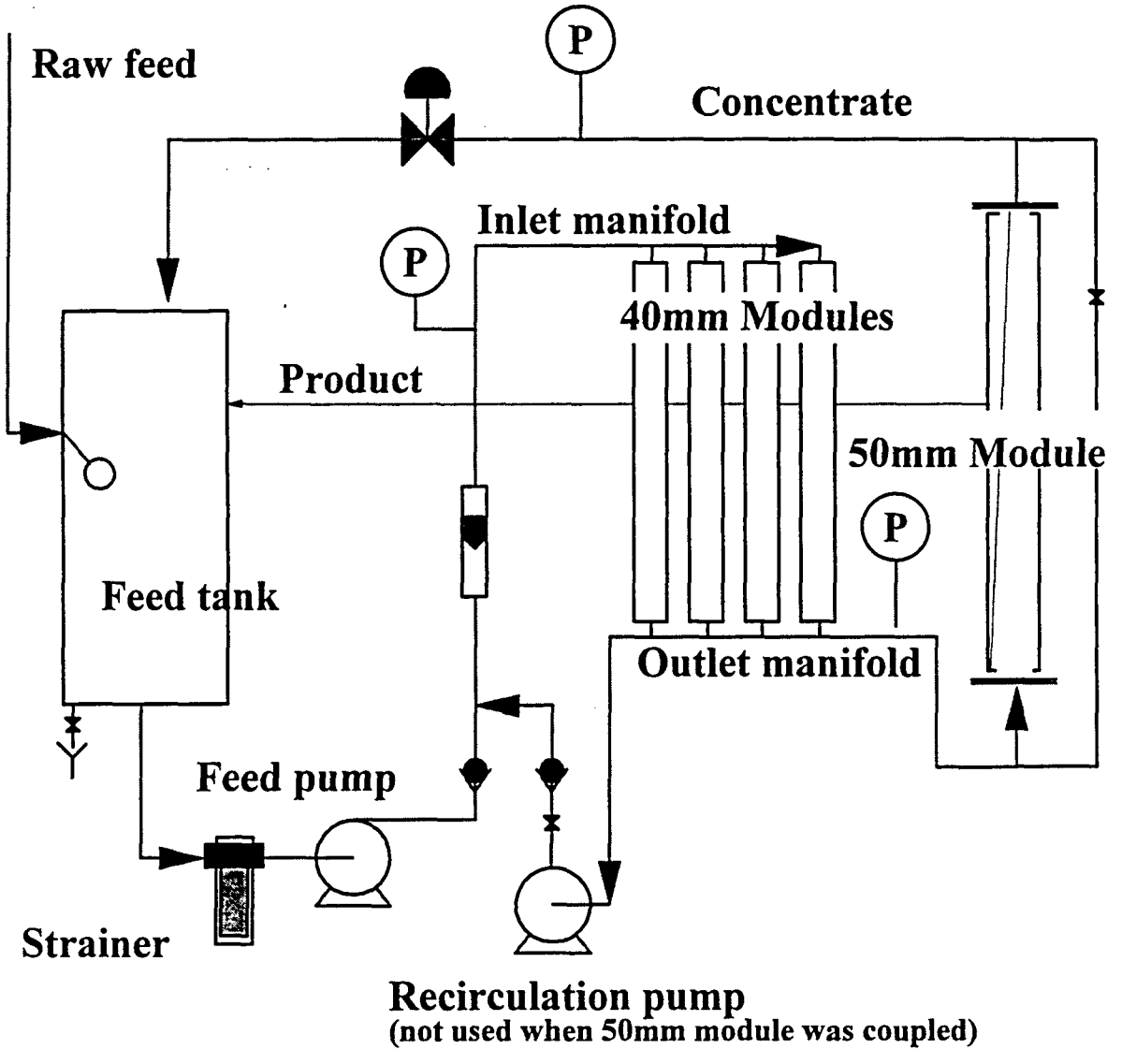

Figure 21: Schematic diagram of the capillary membrane test rig

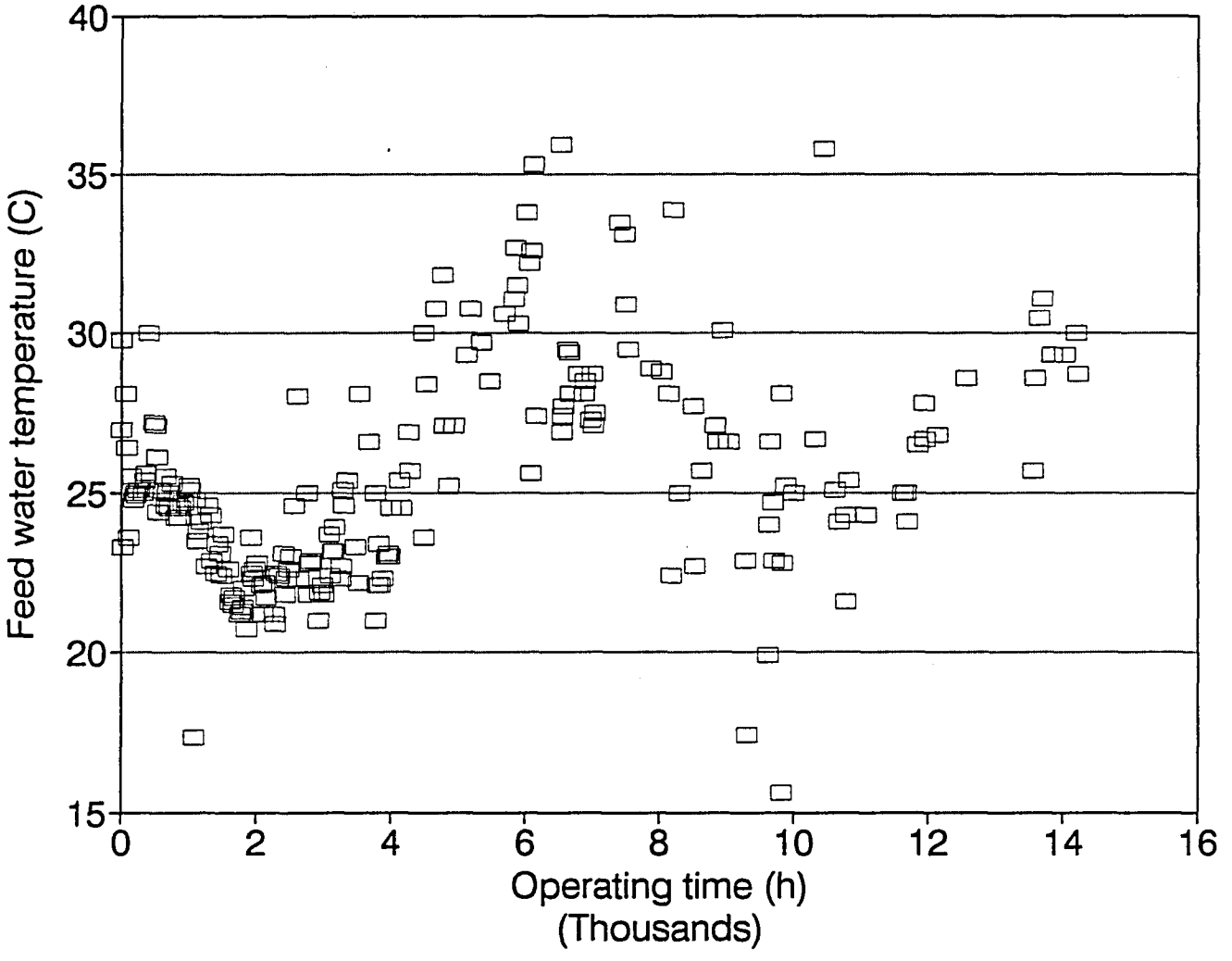

Figure 22: Temperature of the maturation pond effluent feed to the capillary membrane test rig

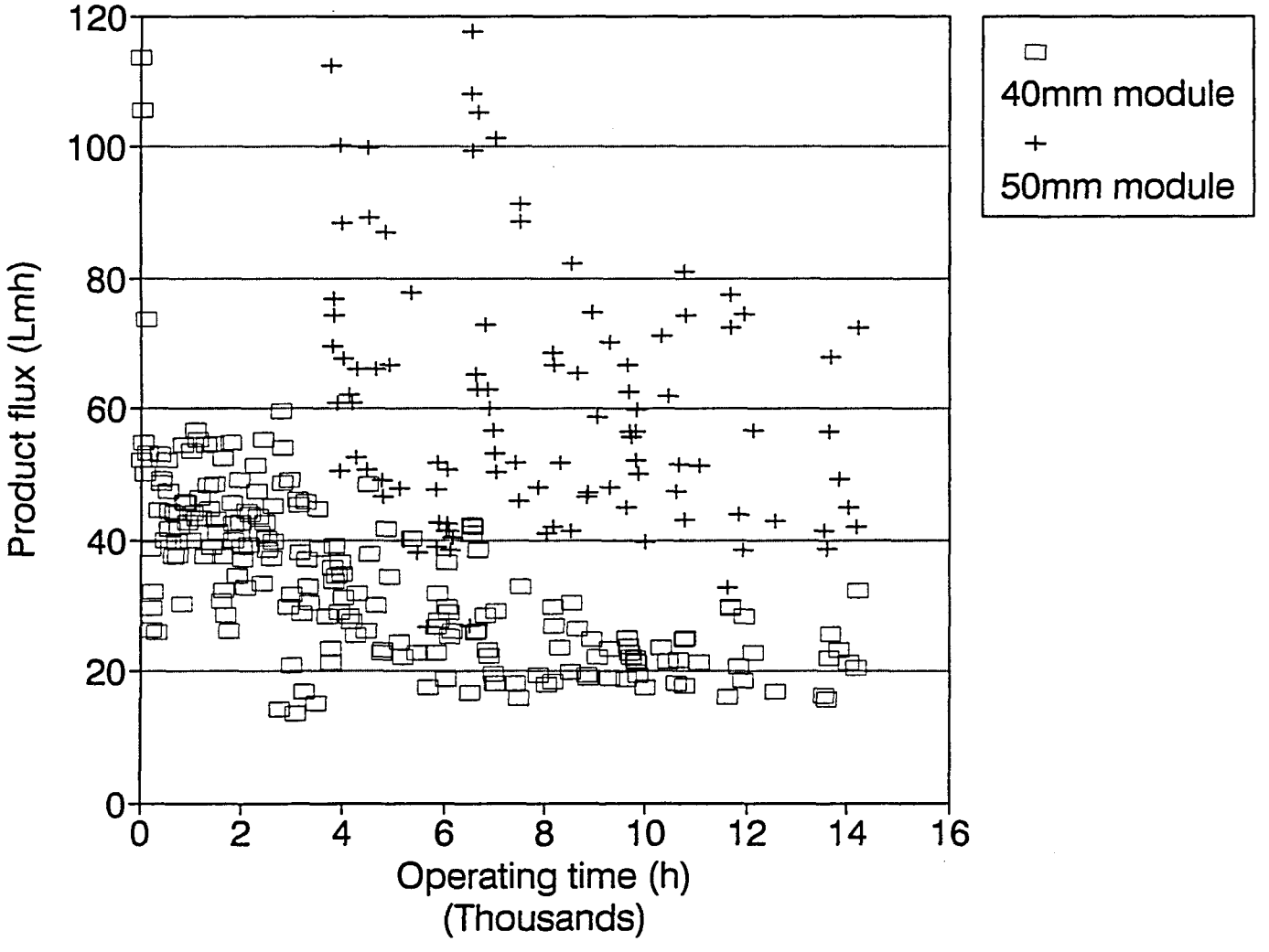

Figure 23: Product flux of the 40mm and 50mm capillary membranes

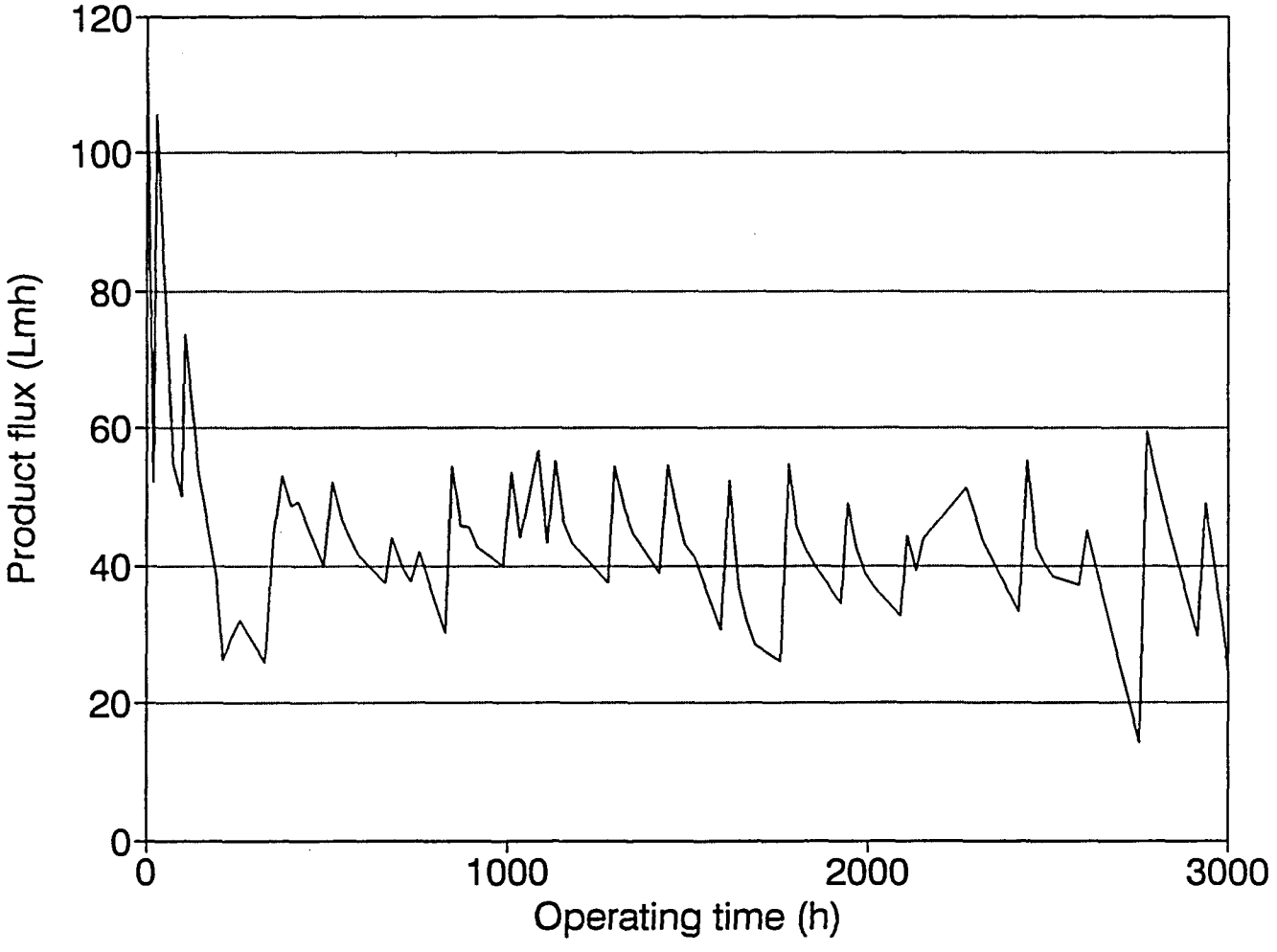

Figure 24: Product flux of 40mm capillary membrane modules over first 3000h of operation

However, module fabrication, membrane morphological considerations and process operation also play roles in membrane flux limitations. Figure 23 shows clearly that the 50mm module outperformed the 40mm modules. Although the membranes both modules were prepared from polyethersulphone, the formulation used to produce the 50mm module membrane was designed to impart slight hydrophilic properties to the membranes. Another important factor in the construction of the two different modules was that the 40mm modules had a transparent shroud, and because the modules were exposed to sunlight for at least part of the day, algal growth had established itself on the outsides of the membranes. A stainless steel shroud was used to encase the membranes in the 50mm module and no algal growth formed on these membranes.

Due to the design of the membrane test plant, no attempts could be made to investigate the effect of intermittant forced backflush on product flux. The system was, however, operated in an on/off mode (60min on, 1min off); 1m static head on the product line. The static back-pressure of 1m was, however, not sufficient to improve the flux performance of the system.

C. Colour removal

The colour of the feed to the ultrafiltration plant is shown in Figure 25 and that of the combined product of the 40mm modules and 50mm module in Figure 26. From these figures it is apparent that the ultrafiltration membranes were capable of reducing the colour content of the water considerably, although nowhere near to the same extent as was achieved with the nanofiltration membranes. The membranes routinely achieved colour retention values exceeding 75%. On average, however, the final product water was still highly coloured and if measured against this variable only, will not be acceptable as a first-grade water. The high colour content of the feed water was probably caused by the presence of textile dye effluent.

D. COD reduction

The ultrafiltration membranes reduced the COD content of the feed water (see Figure 27), but with colour reduction, the performance of these membranes were not as good as that of nanofiltration. A large fraction of the organic species present in the maturation pond effluent was of low molecular mass, and a large reduction in their concentration would not be expected. However, the membranes did reduce COD by about 50%, which could indicate the presence of a secondary membrane-layer on the surface of the capillary membranes (formed

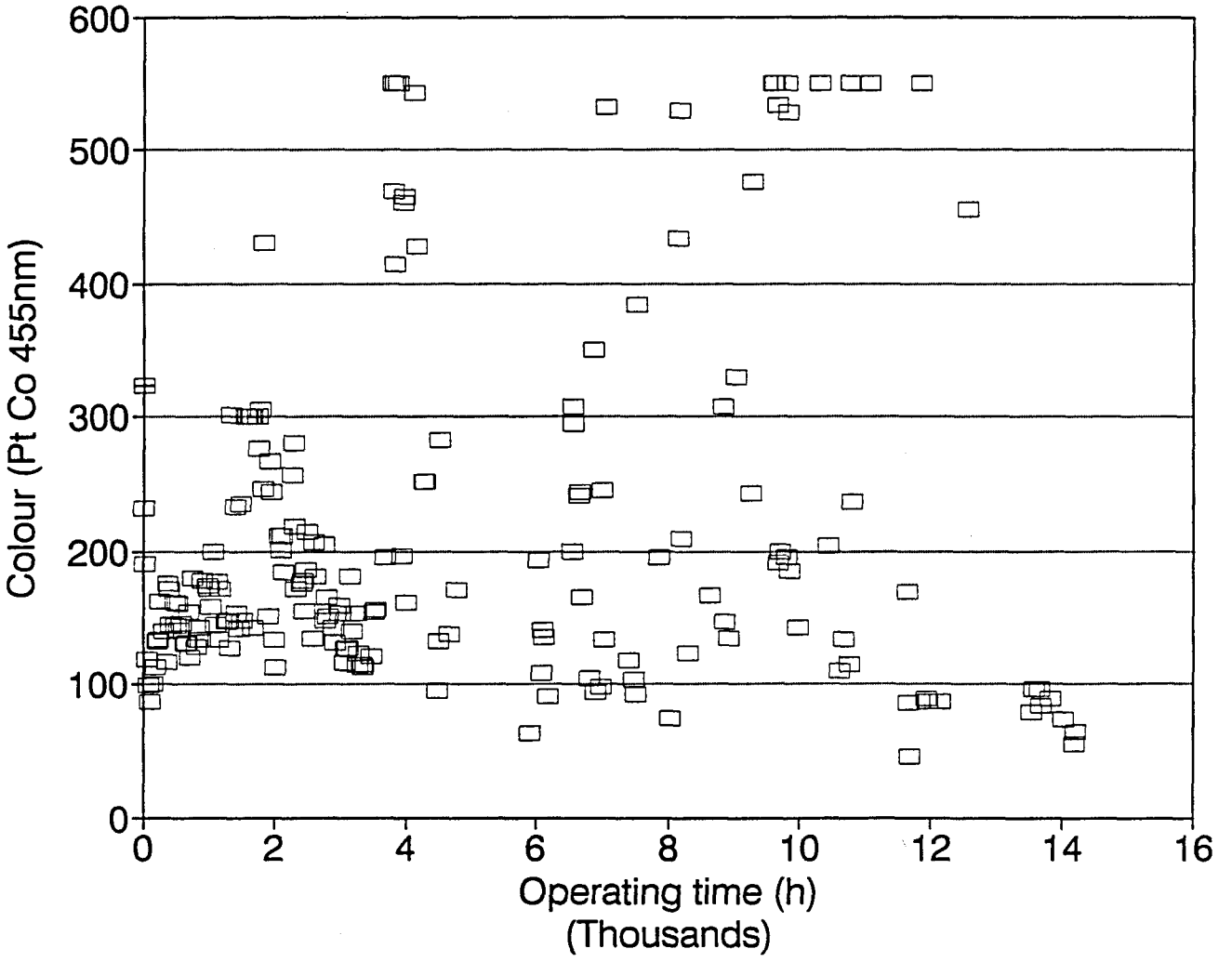

Figure 25: Colour content of the maturation pond feed to the ultrafiltration plant

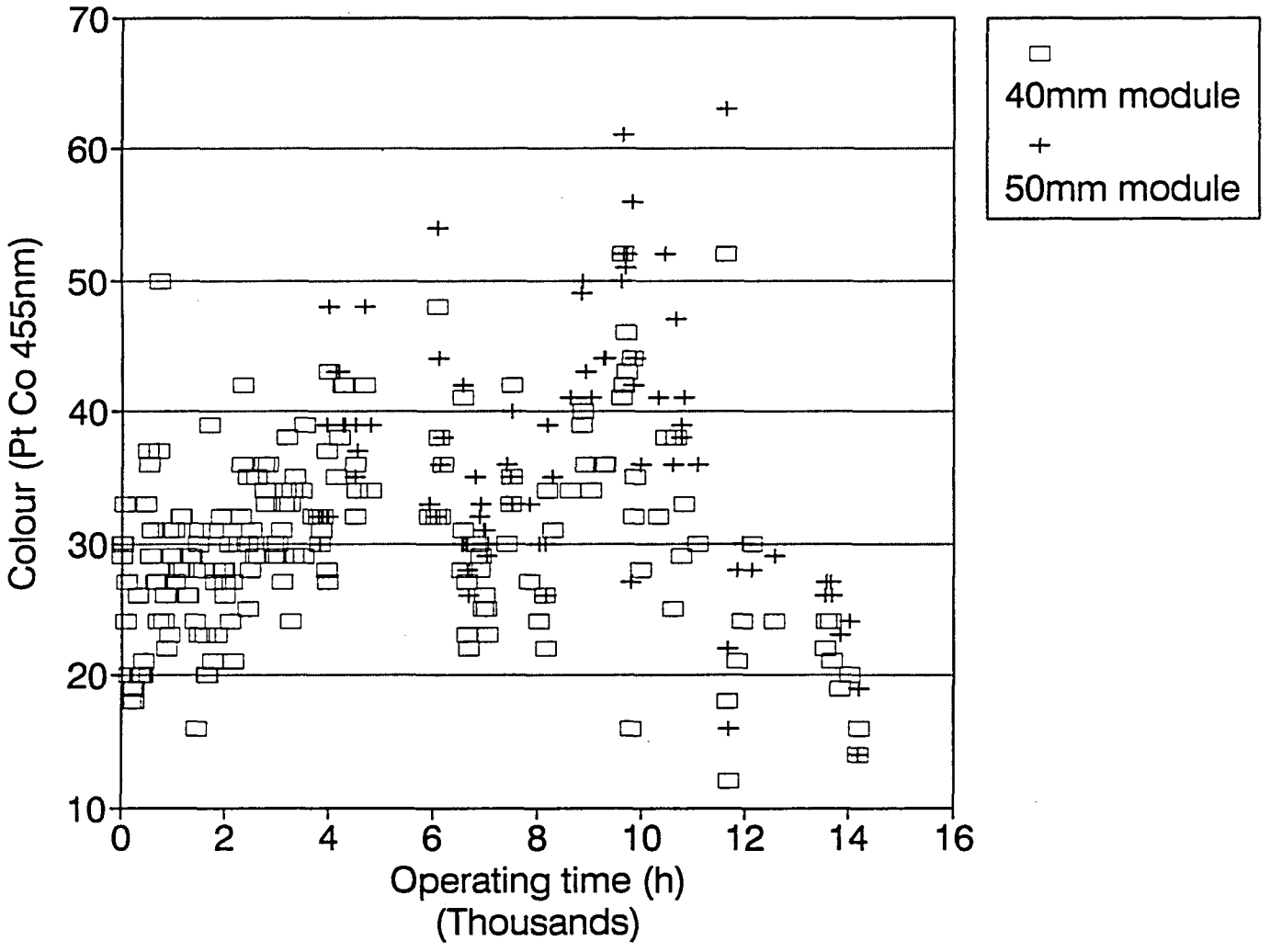

Figure 26: Colour content of the ultrafiltered product

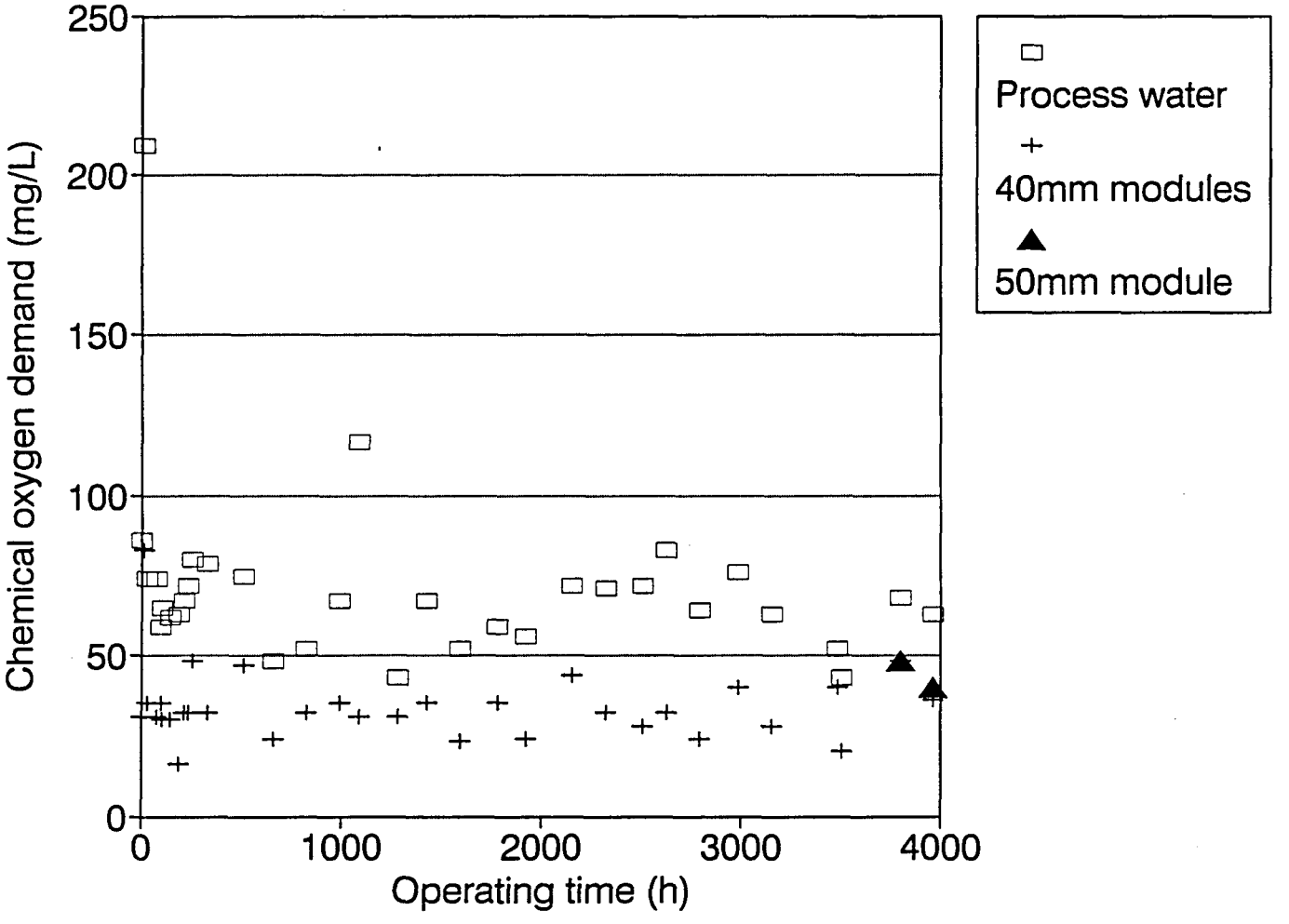

Figure 27: Chemical oxygen demand of the maturation pond feed water and ultrafiltered product

as result of concentration polarization), as well as the presence of larger-sized recalcitrant molecules in the feed water which were not altered in size by the biological treatment operation.

COD measurements were discontinued after 4 000h because of restricted laboratory time allocation for these determinations.

E. Turbidity removal

The ultrafiltration membranes produced a final clear product of very low turbidity as can be seen in Figure 28 which also illustrates that the turbidity of the filtered product is not coupled to the turbidity of the feed water, and that turbidity values of less than 0,2NTU could be achieved consistently. This correlated to turbidity reduction rates greater than 95%.

F. Microbial indicators

The nanofiltration and ultrafiltration membranes did not prove to be a sterile filtration barrier as indicator organisms were found to be present in the filtered product of both processes. This could be due to product line recontamination, that is, reverse infiltration of the organisms through the product output line. It could also be the result of poor membrane manufacture which would result in pin-holes or large-sized pores in the skin-layers of the membranes. However, both membrane filtration processes reduced microbial counts.

If one were to accept this as fact, the question was to what extent did the product water need to be chlorinated to ensure a disinfected product? In one experiment, different concentration levels of chlorine was introduced to 200ml samples of the nanofiltered and ultrafiltered products, and stirred in a closed container for a period of 60min. The residual chlorine was destroyed after this contact period and the samples were tested for the presence of total and feacal coliform plate counts. The data for two experiments are shown in Table 8. From this data it shows that different chlorine demands was necessary to achieve disinfection. The demand decreased in the order feed>ultrafiltered product>nanofiltered product.

G. Cleaning regimes

The poly(ether sulphone) ultrafiltration membranes are hydrolytically more stable than cellulose acetate membranes, and for this reason more stringent cleaning protocolscould be

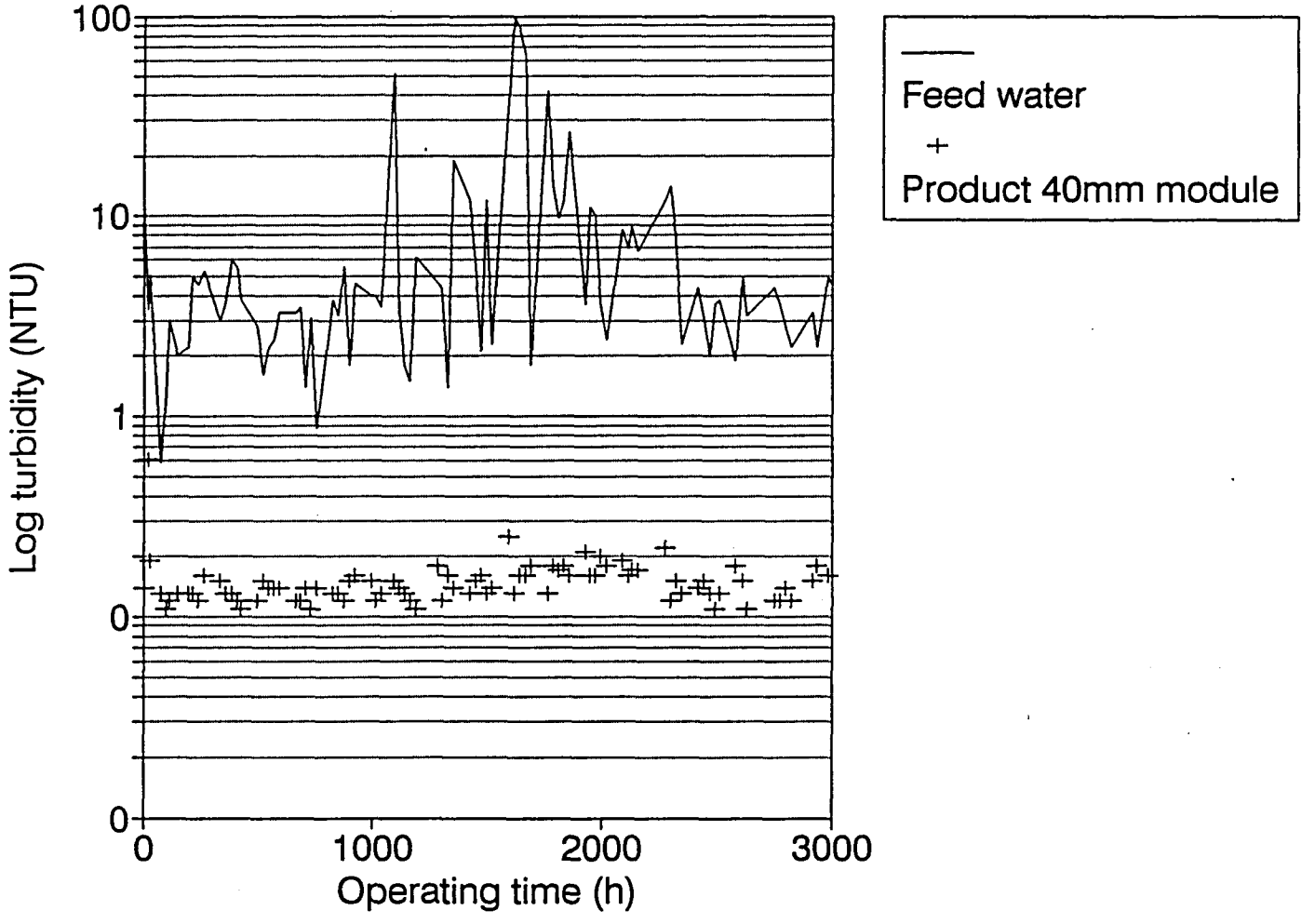

Figure 28: Turbidity removal efficiency of the ultrafiltration process

devised. Table 9 gives a list of the different cleaning procedures used. Unfortunately, although capillary membranes can be backflushed (i.e. by reversing the direction of product flow through the membrane wall), the plant design did not include this option. On occasion, however, individual modules were removed and backflushed manually with tap water for 5min.

Table 8: Chlorine demand of nanofiltered and ultrafiltered product

Sample	Type	Chlorine	Experiment 1		Experiment 2	
		mg/L	Feacal coli	Total coli	Feacal coli	Total coli
1	A	0	14	400+	0	TNC
2	A	2	2	65	0	TNC
3	A	4	2	27	0	24
4	A	6	0	37	0	14
5	A	8	0	37	0	8
6	A	10	0	31	0	1
7	B	0	55	213	0	18
8	B	0.5	1	68	0	17
9	B	1	0	1	0	1
10	B	1.5	0	2	0	0
11	B	2	0	2	0	1
12	B	2.5	0	0	0	0
13	C	0	0	1	0	36
14	C	0.25	0	0	0	3
15	C	0.5	0	2	0	0
16	C	0.75	0	2	0	0
17	C	1	0	1	1	12
18	C	1.25	0	1	0	0

A: Maturation pond effluent, B: 50mm Ultrafiltration module product, C: Nanofiltration product
TNC: too numerous to count

None of the cleaning regimes used had any detrimental effect on the integrity of the membranes, but some permanent flux loss was observed over the full duration of the experiment. This could have been caused by permanent pore blocking or irreversible fouling of the membrane surface. No autopsy was performed on the membranes to determine the reason for low product yields towards the end of the experiment, or of the the poor recovery of product flux after cleaning.

Table 9: Cleaning regimes for ultrafiltration membranes

Protocol	Duration
Clean water rinse	20min
SCL 1g/l	10min
NaOH pH 12 + SCL 1g/l	10min ea
Punch 2%, pH 11	30min
Punch 2%, pH 11	60min
Punch 2%, pH 11	120min
Punch 2% + SCL 1g/l	20min ea
Biotex 2%	60min
Biotex 2% + *Punch* 2%	60min, 120min
Sanochlor 7,5ml/l + EDTA 2g/l	30min, 120min
Biotex 2%	600min
Sanochlor 10g/l	20min
Biotex 2% + *Sanochlor* 10g/l	120min, 30min
Sodium lauryl sulphate 0,5% + *Sanochlor* 1%	90min, 30min
Acid wash pH2 + *Lever Ind LSD64* 1% pH 9.7	10min, 960min
LSD64 1% + acid rinse pH2	120min, 10min
Acid wash pH2 + *LSD64* 1%	10min, 120min
Acid rinse pH2 + *LSD64* 2% pH 9.7	10min, 960min
LSD64 2% pH 9.7	120min
LSD64 2% pH 9.7 + *Sanochlor* 100mg/l + acid rinse	120min, 20min, 10min

V. EVALUATION OF AN ALTERNATIVE DETERGENT AS CLEANING AGENT

A Lever Bros detergent (*LSD64*) was tested as a cleaning agent during the evaluation of the nanofiltration membranes on maturation pond effluent. The flux of the nanofiltration membranes was restored with the new detergent. However, it was deemed necessary to evaluate the detergent on reverse osmosis membranes as well, since it was argued that if the detergent had any adverse effect on membrane performance, reverse osmosis membranes would be more sensitive and would sooner indicate any transient effects on performance.

A study was therefore conducted to compare the effect of prolonged contact with *Biotex* and *LSD64* on the salt-retention and flux performance of cellulose acetate tubular reverse osmosis membranes. The object was to determine whether *LSD64* could be used as a viable alternative or to replace *Biotex* which is the generally recommended and used detergent.

1. EXPERIMENTAL

A. Samples

TRO CA membranes were obtained from Envig (Pty) Ltd. The membranes were taken ar random from the production line after they had been annealed. The membranes were removed before the quality control station at Envig (Pty) Ltd.

B. Test procedure

Six 1m-long membrane sections, connected in series, were tested in the following way:

- Precompaction test: 4h at 4MPa, tested against 2g/L NaCl at a linear velocity of 1m/s and a temperature of 20°C. The salt-retention performance (conductivity retention) and water flux were determined. These results were used as the base-line performance.
- The membranes were next subjected to a pure water flux (PWF) test, in which the membranes were tested against pure water at a feed pressure of 2MPa and linear velocity of 1m/s.
- The feed tank was charged with 0,5% by mass of the selected detergent, without pH adjustment or the addition of any further chemicals. The system was operated at a feed pressure of 2MPa and a linear velocity of 1m/s during the detergent contact cycle of operation.
- The detergent contact test was continued for a day when the feed solution was rinsed from the system and replaced with pure-water. The membranes were again tested against the 2g/L NaCl feed solution and the cycle of tests repeated.
- The tests were terminated after >100h accumulated exposure time.
- Biotex (pH 8.6) and LSD64 (pH 10.3), the latter a product of Lever Industries, Boksburg, were used in the tests.
- The tests were conducted at both 20°C and 30°C.

C. Results

The pure water flux (PWF) performance and the NaCl retention and RO flux performances are shown in Table 10 for the *Biotex* (20°C and 30°C) and *LSD64* (20°C and 30°C) tests.

D. Discussion

Close inspection of the results indicates that the detergents had no significant effect on the performance of the membranes. There is no clear indication that any of the detergents affected membrane performance adversely.

Table 10: Performance of membranes in contact with *Biotex* and *LSD64*

Accum. [h]	RO flux @ 2g/L, 4MPa, 1m/s [Lmd]						RO conducivity retention @ 2g/L, 4MPa, 1m/s [%]						Pure-water flux, 2MPa, 0,5m/s [Lmh]					
	1	2	3	4	Mean	Std. Dev	1	2	3	4	Mean	Std. Dev	1	2	3	4	Mean	Std. Dev
LSD64 20°C																		
0	24.6	30.3	28.3	26.5	27.4	2.1	97.7	96.5	97.6	97.3	97.3	0.5	16.1	20.8	18.8	17.4	18.3	1.7
23.6	23.7	29.3	27	25.4	26.4	2.1	97.9	97.1	98.1	97.8	97.7	0.4	15	18.8	16.9	16.2	16.7	1.4
45.8	24	29.8	27.3	26.2	26.8	2.1	97	96	97.6	97.1	96.9	0.6	14.7	18.6	16.8	16.2	16.6	1.4
71.1	23.4	28.8	26.5	25.4	26.1	2.1	97.3	97	98	97.5	97.4	0.4	14.7	18.2	16.8	16.1	16.5	1.3
117.2	23.7	29.4	28.3	25.8	26.8	2.2	97.2	96.6	97.9	97.5	97.3	0.5	14.7	18.2	16.8	16	16.4	1.3
141.5	24.2	30.1	27.7	26.3	27.1	2.1	97.9	96.5	97.8	97.4	97.4	0.5	14.6	18.2	16.9	15.7	16.3	1.3
159.7													14.5	18.1	16.6	15.8	16.3	1.3
LSD64 30°C																		
0	30.7	26.2	28.4	31.4	29.2	2.1	98.3	98.4	98.4	98.1	98.3	0.1	20.4	16.3	17.4	21.7	19	2.2
23	32.4	25.4	28	31.9	29.4	2.9	98.3	98.4	98	98.1	98.2	0.1	20.5	16.4	17.7	21.8	19.1	2.1
46.1	32.1	25.1	27.2	34	29.6	3.6	98	98.6	98.2	97.9	98.2	0.3	20.7	16.1	17.7	22	19.1	2.3
69.4	32	25.1	27.3	34.2	29.6	3.6	98	98.6	98	97.8	98.1	0.3	20.7	15.9	17.6	22.1	19.1	2.4
92.7	32.7	25.3	27.5	34.7	30.1	3.8	97.9	98.6	98	97.8	98.1	0.3	20.9	16.2	17.7	22.3	19.3	2.4
112.3													21.5	16.4	18	22.8	19.7	2.6
Biotex 20°C																		
0	24	25.1	24.8	22.1	24	1.2	95	97.2	97.8	97.3	96.8	1.1	18.9	19.3	19.2	16.6	18.5	1.1
22.8	24.6	25.8	25.1	22.7	24.6	1.2	97.9	97.1	98.1	97.8	97.7	0.4	17.2	16.9	16.4	14.7	16.3	1
45.1	23.5	24.5	23.9	21.6	23.4	1.1	96	97.7	97.2	98.3	97.3	0.8	16.2	16.8	16.3	14.6	16	0.8
68.8	24	25	24.4	22.2	23.9	1	95.7	97.8	97.2	98.3	97.2	1	16.2	16.6	16.2	14.4	15.9	0.9
116.5	23.6	24.7	23.9	21.7	23.5	1.1	95.9	97.7	97.1	97.5	97.1	0.7	15.7	16.4	16	14.2	15.6	0.8
139.6	23.8	24.8	24.4	22	23.7	1.1	95.3	97.6	96.9	98.2	97	1.1	15.8	16.2	15.8	14.2	15.5	0.8
159.2													15.6	16.1	15.8	14.2	15.4	0.7
Biotex 30°C																		
0	27.2	31.9	33.1	29.4	30.4	2.3	98.7	98.4	98.4	98.5	98.5	0.1	17.1	20.5	21.2	18.9	19.4	1.6
25.4	26.3	31.2	32.9	29	29.8	2.4	95.7	98.3	98.2	98.4	97.6	1.2	17.7	21	22	19.6	20.1	1.6
50.2	26.2	30.7	32.5	28.5	29.5	2.4	97.1	98.4	98.3	98.5	98.1	0.6	17.1	20.4	21.5	18.8	19.5	1.7
72.7	26.2	30.7	32.5	27	29.1	2.6	97.1	98.1	98	98.2	97.8	0.4	17	20.1	21.3	18.8	19.3	1.6
96.5	25.4	29.5	31.3	27.9	28.5	2.2	98.4	98.2	97.9	98.1	98.2	0.2	16.2	18.5	19.7	17.7	18	1.3
1148													16.8	19.7	20.8	18.5	18.9	1.5

VI. CONCLUSIONS

- ❑ The ultrafiltration capillary and nanofiltration tubular membranes performed well during the studies and no problems were experienced with their integrity over the 16 000h period tested.
- ❑ The turbidity of the ultrafiltered product was very low. The membranes showed good colour-removal capabilities, but the colour of the filtered product was still higher than the maximum specified for potable water.
- ❑ The COD load in the ultrafiltered product was low, but not as low as that in the nanofiltered product.
- ❑ The flux performances of the 40mm and 50mm modules did not correspond. The membranes were produced from the same formulation, but the fabrication protocol was slightly different. It should therefore be possible to improve the flux performance of the capillary membranes, without decreasing the retention performance, by modifying the membrane formulation and fabrication protocol.
- ❑ The 40mm capillary membrane cartridge modules performed well. No leaks occurred between the tubesheet and the module shroud as the seal remained intact. The design of the 50mm stainless steel capillary membrane cartridge module also proved to be adequate to sustain long-term use.
- ❑ The stainless steel shroud of the 50mm module proved to be an advantage as no algal growth appeared on these membranes, as happened to the 40mm modules which had transparent shrouds.
- ❑ u-PVC proved to be an adequate and inexpensive material for use in the construction of module shrouds. However, the u-PVC material did impose an upper operating temperature limit of 40°C.
- ❑ The performance of the nanofiltration membranes declined with time. This was ascribed to hydrolysis of the cellulose acetate membranes as no acid was used to adjust the pH of the feed water to a more suitable level.
- ❑ The quality of the nanofiltered water was very high, and nanofiltration could be useful for the treatment of secondary treated sewage, to produce high quality water for industrial use.

VII. RECOMMENDATIONS

The capillary ultrafiltration membranes performed well during the experiments and their relevance in potable water production and effluent treatment should be investigated further. There are, however, aspects of the present technology that should receive attention. These are summarized below:

- ❑ Membrane fouling could be a deterent in the use of membrane filtration technology. The development of *antifouling* precoats should be investigated as it would not only shorten intervals between membrane cleaning, but would also

reduce the harshness of the protocol required to clean the membranes. This applies equally to nanofiltration and ultrafiltration.

- ❑ Low-cost modules and manifolding should be developed. Special attention should be given to increasing the membrane area in these modules. The modules and manifolding system should be designed so as to simplify module removal for ease of membrane replacement and other reasons.
- ❑ The use of ultrafiltration to upgrade industrial effluents should be investigated on a larger scale (20 to 40m^2 membrane area).
- ❑ The use of ultrafiltration to upgrade surface water to standards set for drinking water should be investigated on a larger scale. The possibility of using a standard approach to the treatment of waters with different turbidities should be investigated. It is very important that indicator micro-organisms should be monitored very regularly during such experiments so as to determine the efficiency of the membranes as absolute filtration barriers.
- ❑ Attention should be given to the development of a standardized microbial or virus indicator test to monitor the removal/reduction efficiency of ultrafiltration membranes in potable water production applications or as a quality control measure during membrane manufacture.
- ❑ A cost study should be conducted to determine the specific cost to treat surface water to drinking water standards.

VIII. TECHNOLOGY TRANSFER

The results obtained in this study indicated that the capillary ultrafiltration membranes and module prototypes developed at the Institute of Polymer Science were useful for water clarification and colour reduction. As an extention of the work conducted in this programme, the ultrafiltration membranes were tested in larger-sized modules at Mon Villa (WRC project KV/184: *Research on rural and peri-urban water supply*). The 90mm modules used had a membrane area of 4m^2 and were an upscaled version of the 40mm module design tested at Uitenhage. The inlet and outlet manifolds of the 90mm modules had similar T-piece designs similar to those used at Uitenhage.

The results of the trials at Mon Villa demonstrated the usefulness of ultrafiltration capillary membranes as a one-step treatment option for potable water production. The raw water treated at Mon Villa had an incoming colour content that ranged between 40 and 60 Hazen units. A surprising result was that the membranes were capable of producing a final water with a colour content below 5 Hazen. These results lead to further investigations and in a collaborative WRC programme (WRC project K5/764: *Research into water supply to rural and peri-urban communities using membrane technologies*), which involved co-operation

from the Chemical Engineering Department of ML Sultan Technikon, it was demonstrated, at Suurbraak in the South Cape, that the membrane process was capable of reducing the colour content of the incoming water from Hazen colour units of as high 600 to values of below 10. The water recovery ratios achieved at Suurbraak often exceeded 85%, and in which case the concentrate had colour values exceeding 2000 Hazen units.

A pilot plant operating on six 90mm capillary ultrafiltration membrane modules is currently being tested at the Windhoek Goreangab reclamation plant, to determine the capability of the membranes to remove protozoan cysts and o-ocysts from the reclaimed water. The membranes are producing good quality water, with turbidity values often as low as 0,06 NTU.

Although the ultrafiltration process is still under development and much R&D is essential to improve the membranes, modules and process, Umgeni Water has expressed an interest in commercializing the technology. A pilot plant which can acommodate up to twelve 90mm modules has been constructed by Umgeni Water, in collaboration with the Chemical Engineering Department of ML Sultan Technikon, to test the process on various feed waters.

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INVESTIGATION TO UPGRADE SECONDARY TREATED SEWAGE EFFLUENT BY MEANS OF ULTRAFILTRATION AND NANOFILTRATION FOR MUNICIPAL AND INDUSTRIAL USE

Final Report to the

Water Research Commission

by

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The various contributions of members of the staff at the sewage works is also appreciated. We are also thankful for the assistance of the laboratory staff at the sewage works with sample analysis. The work of **Ms HC Kleinhans**, in particular, has found its way into many of the tables and figures presented in the report.

Executive Summary

Objectives

The objectives of the research were to determine to what extent medium-molecular-mass cut-off capillary ultrafiltration and tubular nanofiltration membranes, developed at the Institute of Polymer Science of the University of Stellenbosch, could be used to improve the quality of secondary treated sewage and water from the Orange/Fish River scheme. It was not intended to develop a membrane-treatment process, but rather to evaluate the performance and integrity of the nanofiltration membranes and capillary membranes and modules over an extended period of operation, under specific operating conditions.

Objectives not addressed

According to the original contract, the ultrafiltration and nanofiltration membranes and modules were to be tested on secondary-treated sewage as well as on Orange River water. At the time that the contract proposals were submitted, concern was being expressed by Uitenhage industrialists regarding the hardness and colour content of the Orange River water delivered to Uitenhage via the Fish River Tunnel scheme. The initial problem with regards to hardness and colour improved considerably and was found more acceptable once water was drawn continuously from the Orange River Scheme and, after treatment, was blended with indigeneous water. This made treatment by means of ultrafiltration and nanofiltration unecessary and resulted in neither of the membrane processes being tested on Orange River water.

However, this did not detract from the need to assess ultrafiltration as a possible one-step treatment operation to clarify and purify surface water to standards set for potable water.

The opportunity to test the capillary membrane ultrafiltration process on surface water arose at Mon Villa (the then seminar centre of the University of Stellenbosch), whose only consistent source of water was irrigation water from the Theewaterskloof/Helderberg irrigation scheme (WRC project KV/184: *Research on rural and peri-urban water supply).*

This programme showed over a period of more than 20 000h that capillary ultrafiltration membranes can be used to provide high-quality drinking water in a one-step operation without the addition of chemicals.

Because of the limited membrane area and feed-tank holding volumes of the bench-scale membrane plants at Uitenhage, problems arose with heat build-up during recirculation. Recovery ratios had therefore to be kept low during the experiments at Uitenhage. (This problem was overcome at the Mon Villa site where a 4 500l feed tank and much larger membrane capacity was installed. Recovery ratios exceeding 95% were regularly achieved during those experiments, without any permanent loss in membrane flux performance).

Membranes and modules

The capillary membranes and modules which were to be tested were the research products of WRC Project No. 387 entitled: *The development and production of membrane systems.* The ultrafiltration capillary membranes (coded #748) that were developed during this research programme were fabricated from poly(ether sulphone). The membranes had a molecular-mass cut-off of 35 000 dalton (tested on polyethylene glycol) and were internally skinned. Two module prototypes were developed during WRC Project No. 387 to house the capillary membranes. The one module, a 40mm-diameter cartridge-type module with a transparent uPVC shroud, was secured in a manifold fabricated from standard uPVC T-pieces and sealed by means of O-rings. The other, a 50mm module with a stainless steel shroud, was flange-mounted.

The tubular cellulose acetate membranes which were to be tested were also the research products of WRC Project No. 387. These membranes were housed in PCI modules. The modules were fitted with perforated stainless steel tubes and sealed on either side with rubber grommets. Eighteen 2,4m-long membranes were connected in series in each of these modules.

CONCLUSIONS

- The ultrafiltration capillary and nanofiltration tubular membranes performed well during the studies and no problems were experienced with their integrity over the 16 000h period tested.

- The turbidity of the ultrafiltered product was very low. The membranes showed good colour-removal capabilities, but the colour of the filtered product was still higher than the maximum specified for potable water.

- The COD load in the ultrafiltered product was low, but not as low as that in the nanofiltered product.

- The flux performances of the 40mm and 50mm modules did not correspond. The membranes were produced from the same formulation, but the fabrication protocol was slightly different. It should therefore be possible to improve the flux performance of the capillary membranes, without decreasing the retention performance, by modifying the membrane formulation and fabrication protocol.

- The 40mm capillary membrane cartridge modules performed well. No leaks occurred between the tubesheet and the module shroud as the seal remained intact. The design of the 50mm stainless steel capillary membrane cartridge module also proved to be adequate to sustain long-term use.

- The stainless steel shroud of the 50mm module proved to be an advantage as no algal growth appeared on these membranes, as happened to the 40mm modules which had transparent shrouds.

- u-PVC proved to be an adequate and inexpensive material for use in the construction of module shrouds. However, the u-PVC material did impose an upper operating temperature limit of 40°C.

- The performance of the nanofiltration membranes declined with time. This was ascribed to hydrolysis of the cellulose acetate membranes as no acid was used to adjust the pH of the feed water to a more suitable level.

- The quality of the nanofiltered water was very high, and nanofiltration could be useful for the treatment of secondary treated sewage, to produce high quality water for industrial use.

RECOMMENDATIONS

The capillary ultrafiltration membranes performed well during the experiments and their relevance in potable water production and effluent treatment should be investigated further. There are, however, aspects of the present technology that should receive attention. These are summarized below:

- Membrane fouling could be a deterent in the use of membrane filtration technology. The development of *antifouling* precoats should be investigated as it would not only ~~shorten~~ lengthen intervals between membrane cleaning, but would also reduce the harshness of the protocol required to clean the membranes. This applies equally to nanofiltration and ultrafiltration.

- Low-cost modules and manifolding should be developed. Special attention should be given to increasing the membrane area in these modules. The modules and manifolding system should be designed so as to simplify module removal for ease of membrane replacement and other reasons.

- The use of ultrafiltration to upgrade industrial effluents should be investigated on a larger scale (20 to 40m^2 membrane area).

- The use of ultrafiltration to upgrade surface water to standards set for drinking water should be investigated on a larger scale. The possibility of using a standard approach to the treatment of waters with different turbidities should be investigated. It is very important that indicator micro-organisms should be monitored very regularly during such experiments so as to determine the efficiency of the membranes as absolute filtration barriers.

- Attention should be given to the development of a standardized microbial or virus indicator test to monitor the removal/reduction efficiency of ultrafiltration membranes in potable water production applications or as a quality control measure during membrane manufacture.

- A cost study should be conducted to determine the specific cost to treat surface water to drinking water standards.

TECHNOLOGY TRANSFER

The results obtained in this study indicated that the capillary ultrafiltration membranes and module prototypes developed at the Institute of Polymer Science were useful for water clarification and colour reduction. As an extention of the work conducted in this programme, the ultrafiltration membranes were tested in larger-sized modules at Mon Villa (WRC project KV/184: *Research on rural and peri-urban water supply*). The 90mm modules used had a membrane area of $4m^2$ and were an upscaled version of the 40mm module design tested at Uitenhage. The inlet and outlet manifolds of the 90mm modules had similar T-piece designs similar to those used at Uitenhage.

The results of the trials at Mon Villa demonstrated the usefulness of ultrafiltration capillary membranes as a one-step treatment option for potable water production. The raw water treated at Mon Villa had an incoming colour content that ranged between 40 and 60 Hazen units. A surprising result was that the membranes were capable of producing a final water with a colour content below 5 Hazen. These results lead to further investigations and in a collaborative WRC programme (WRC project K5/764: *Research into water supply to rural and peri-urban communities using membrane technologies*), which involved co-operation from the Chemical Engineering Department of ML Sultan Technikon, it was demonstrated, at Suurbraak in the South Cape, that the membrane process was capable of reducing the colour content of the incoming water from Hazen colour units of as high 600 to values of below 10. The water recovery ratios achieved at Suurbraak often exceeded 85%, and in which case the concentrate had colour values exceeding 2000 Hazen units.

A pilot plant operating on six 90mm capillary ultrafiltration membrane modules is currently being tested at the Windhoek Goreangab reclamation plant, to determine the capability of the membranes to remove protozoan cysts and o-ocysts from the reclaimed water. The membranes are producing good quality water, with turbidity values often as low as 0,06 NTU.

Although the ultrafiltration process is still under development and much R&D is essential to improve the membranes, modules and process, Umgeni Water has expressed an interest in commercializing the technology. A pilot plant which can acommodate up to twelve 90mm

modules has been constructed by Umgeni Water, in collaboration with the Chemical Engineering Department of ML Sultan Technikon, to test the process on various feed waters.

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Investigation to upgrade secondary treated sewage effluent by means of ultrafiltration and nanofiltration for municipal and industrial use

I. INTRODUCTION

Water is a scarce and precious commodity in Southern Africa. In many parts of this region the available surface and subsurface resources are nearly, or are already being, exploited to capacity. In certain areas water is being redirected from one catchment area to supplement that in another, whereas in others, for example Windhoek in Namibia, secondary treated sewage is recovered to augment available supplies. A treatment technology was developed in Windhoek by which the quality of the sewage that was treated by conventional technology could be upgraded to comply with standards for potable water. Small quantities of this water are recycled for domestic and drinking purposes.

The Eastern Cape is often faced with droughts and consequently with serious water-shortage problems. This problem has been overcome to some extent by diverting water by tunnel from the Orange River to the Fish River to augment regional supplies. The Cape Peninsula is faced with another problem. Because of the rate of urbanization and the limited number of sites available for construction of dams, serious water shortages are forecast for the region in the short term, with little alternative but to turn to unconventional resources in the longer term. Sea water desalination offers one possibility for providing potable water; another is to use tertiary treated domestic sewage for industrial and domestic applications.

No technology has been implemented in Southern Africa or elsewhere to recover high percentages of secondary treated sewage to provide high quality water for potable use. In this regard membrane filtration could provide another technological option for improving the quality of secondary treated sewage to a stage at which larger volumes of municipal effluent could be recycled.

Different cross-flow pressure-driven membrane processes fulfill different functions. Microfiltration membranes remove suspended solids and reduce bacteriological activity, but will not reduce the colour or dissolved organic content of the water. Ultrafiltration, in which a finer membrane filter is used, will remove medium-molecular-mass dissolved organics and reduce turbidity to levels of 0,1NTU, but can not desalinate water. Nanofiltration membranes

which are even finer can partly desalinate water (soften it, so to speak) and remove substantial quantities of low-molecular-mass organic materials as well as viruses. However, reverse osmosis can be used to produce higher quality filtrates by the use of increased operating or driving pressures to effect separation. Table 1 gives some indication of operating pressure ranges for these pressure-driven membrane processes.

Table 1: Lower operating pressure limits for pressure-driven membrane operations

Microfiltration	Ultrafiltration	Nanofiltration	Reverse osmosis
0,2 bar	1 bar	5 bar	10 bar

II. SCOPE

Two newly developed membrane systems were evaluated in an application to improve the quality of secondary treated sewage effluent from the Uitenhage treatment works. The membrane plants drew their water from the maturation pond. The membranes would furthermore be operated under conditions of limited pretreatment

- An important aspect of the work was to determine the durability and integrity of the poly(ether sulphone) ultrafiltration capillary membranes that were developed for the purpose, and to reach some conclusion about the life-expectancy of these membranes. Various ultrafiltration module and manifold configurations were also evaluated with a view to directing future research and development of larger-sized modules.
- It was also important to obtain some knowledge regarding the operability of the membranes on maturation-pond waters. The performance of tubular cellulose acetate nanofiltration (NF) membranes was to be evaluated over an extended period of time in order to determine performance data and fouling tendencies.
- *Biotex* is often recommended as a useful detergent for cleaning fouled membranes, but it is not supplied in bulk. Another detergent that is available in bulk quantities was evaluated as an alternative cleaning reagent for cellulose acetate nanofiltration membranes.

1. WATER BALANCE AT UITENHAGE

Uitenhage draws its water from three main sources: the Groendal dam, natural springs and the Orange River via the Fish River Tunnel. The latter water is treated by Port Elizabeth Municipality (PEM) before it is distributed to Uitenhage. The water from the Groendal dam and springs is treated by the Uitenhage Municipality. Table 2 gives an approximate indication of water consumption rates over a period of six years, and Table 3 gives an

approximate indication of the volume of water returned to the sewage works during wet and dry periods. A total of 1Ml/d treated sewage is presently being used to irrigate sportsfields and by industry as cooling water.

Uitenhage has a diversity of industries ranging from motorcar manufacture to the fabrication of export-quality knitwear. These industries are placed under severe pressure to reduce their water consumption during periods of severe drought which appear to come in 10-year cycles, (see Figure 1). Larger volumes of water may be drawn by way of Port Elizabeth Municipality from the Fish River scheme, but from the analysis shown in Table 4 it can be deduced that the quality of this water is lower than that of water from indigenous resources. Industry will therefore be forced during periods of severe drought to introduce point-source treatment, such as water softening, before the water can be used. If this happens, an alternative would be to re-use secondary treated sewage.

Table 2: Comparison of Uitenhage water consumption rates (annual)

Water source	90/91	91/92	92/93	93/94	94/95	95/96
			Daily Average in Ml			
Groendal dam	11.34	6.91	8.88	10.14	10.25	10.99
Natural springs	4.03	3.87	3.86	4.02	4.29	4.5
PEM (Orange river)	6.23	5.32	3.44	3.09	3.21	1.61
Total	21.6	16.1	16.18	17.25	17.75	17.1

Table 3: Effluent returned to the sewage works for treatment

Effluent source	Normal conditions	Dry conditions
	Ml/day	
Industries	8	6
Domestic (Uitenhage)	8	6
Kwanobuhle	4	3
Total	20	15

The Uitenhage city planners allowed for secondary treated water supply to parts of the industrial sector of the town. A dam was constructed in the higher regions and an estimated 1Ml secondary treated sewage is pumped into this dam from where it gravitates back into the

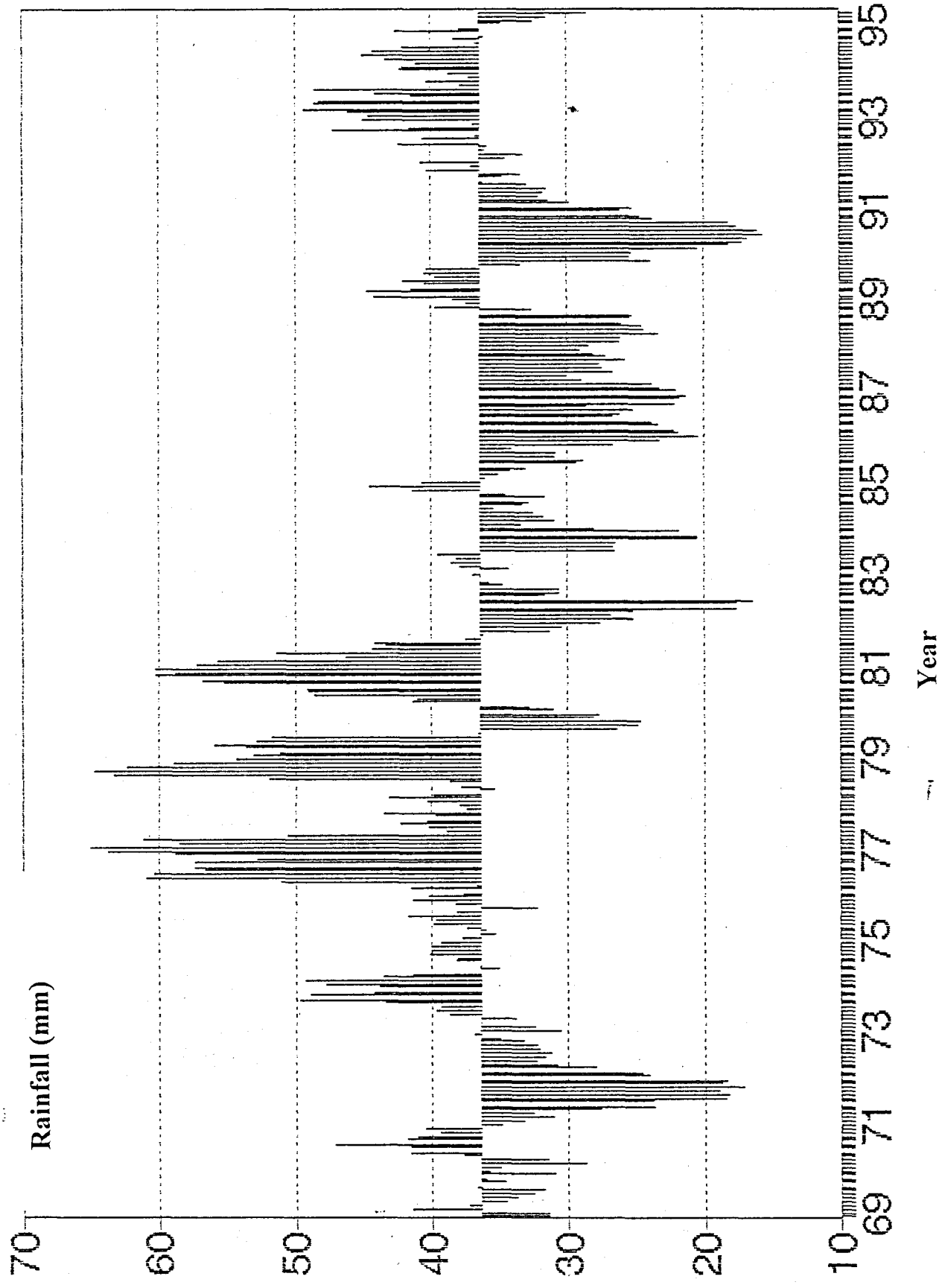

Figure 1: Rainfall statistics for Uitenhage over a 10-year period

industrial area. Uitenhage is therefore ideally suited to investigate the usefulness of membranes in this tertiary treatment role.

Table 4: Comparison of compositions of indigenous and imported water

23 January 1994	Groendal raw	Groendal final	Springs final	PEM
pH	5.89	7.8	4.84	7.13
TDS (mg/l)*	125	150	101	613
Conductivity (mS/m)	19	21	17	103
Colour (Pt C0 @ 455nm)	72	19	3	5
Turbidity (NTU)**	1.9	0.66	0.26	0.56
Total hardness***	21	38	20	260
Calcium (Ca^{++})***	8	27	7	104
Magnesium (Mg^{++})***	13	11	13	156
Total alkalinity***	6	15	4	214
Carbonate alkalinity***	0	0	0	0
Bicarbonate alkalinity***	6	15	4	214
Sodium (Na^{+})	23	23	19	154
Potassium (K^{+})	1.2	1.15	0.4	6.8
Iron (Fe^{+++})	0.41	0.06	0.02	0.09
Aluminium (Al^{+++})	0.07	0.41	0.07	0
Manganese (Mn^{++})	0.01	0.03	0.1	0
Chloride (Cl^{-})	39	41	36	135
Sulphate ($SO^{=}_{4}$)	0	16	0	108
Ammonia (NH_4)	0.19	0.07	0	0.04
Nitrate (NH_3)	0.3	0.4	0.5	0.5
Silica (SiO_2)	6.3	6.3	11.5	10.1
OA (mg/L)	6.8	4	0.2	12.6

*Total dissolved solids (TDS) **Nupheleometric turbidity units (NTU) *** as $CaCO_3$

However, although a large proportion of the industrial area is reticulated to receive this secondary treated sewage to reduce fresh-water intake by industry, the volume of reclaimed water currently used is not high. The quality of the reclaimed water is also not high and, as can be seen from Table 5, the water is essentially fit only for use in cooling and non-sensitive processing. It is reasonable to believe that the quality of the secondary treated water will deteriorate further during periods of drought because of intake of higher volumes of water from Port Elizabeth Municipality. The current permit from the Department of Water Affairs states that at least 80% of the water drawn from the Groendal dam must be discharged after treatment into the Swartkops River.

Table 5: Monthly average performance data of the Kelvin Jones Sewage Works

	+COD (mg/l)		++SS (mg/l)		+++Cond (mS/cm)		NH_3		NO_3
Month	Raw	Fin	Raw	Fin	Raw	Fin	Raw	Fin	Fin
1992									
July	1369	68	516	16	261	219	46	2	3.1
Aug	1354	66	641	14	258	218	40	2	2.5
Sept	1212	65	461	14	228	189	38	2	1.3
Oct	1280	71	469	18	240	201	33	1	4
Nov	1118	59	567	14	254	216	29	0	6.7
Dec	986	61	424	8	208	174	35	0	4.6
1993									
January	1333	56	535	7	181	145	32	1	2.7
February	1271	57	546	5	173	140	33	1	2.8
March	867	60	372	5	174	138	33	1	2.7
April	974	65	494	14	217	172	21	2	4.3
May	1033	68	419	13	198	162	30	2	7.3
June	1134	70	493	14	209	170	44	2	5.1
July	1023	87	379	18	226	186	53	5	1.9
August	1133	63	456	10	217	170	54	4	0.5
September	1008	63	398	11	227	191	44	4	3.3
October	1095	60	458	14	268	230	44	4	2.5
November	1328	59	691	13	224	190	43	7	0.6
December	1411	67	865	13	255	209	43	5	0.9
1994									
January	1083	61	749	13	212	182	27	4	1.6
February	972	60	410	11	207	179	39	4	0.7
March	893	61	373	11	205	178	39	1	0.8
April	851	55	372	9	180	153	42	1	3.3
May	1171	64	493	11	217	180	46	1	3.1
June	1040	80	423	16	231	198	44	1	0.8
July	951	86	364	20	238	204	44	2	3.4
August	839	77	341	16	268	229	36	2	1.7
September	929	69	374	13	231	201	43	2	0.2
October	864	57	357	10	207	180	39	2	0.2
November	895	50	389	8	174	148	37	3	0
December	808	49	423	9	171	143	35	2	0.2

+Chemical oxygen demand (COD) ++Suspended solids (SS) +++Conductivity (Cond)

If one considers that the water drawn from the Groendal dam is augmented from other sources, that is PEM and the Springs, a substantially greater proportion of water can be re-used than at present. However, the low quality of the secondary water is a deterrent.

2. MEMBRANE FILTRATION OPERATIONS

A. Ultrafiltration

Ultrafiltration is a pressure-driven membrane separations operation used to remove dissolved and suspended (particulate and colloidal) macromolecular species from water. Small pores in the skin layer of ultrafiltration membranes enable separation to be achieved by a sieving mechanism whereby dissolved or suspended species that are larger than the pores in the skin layer are retained while those that are smaller will pass through the membrane.

Ultrafiltration is capable of reducing the viral and bacterial counts in water to acceptable levels since the pores in these membranes range in diameter from 2 to 30nm, depending on the molecular-mass cut-off (MMCO) of the membrane. However, the sizes of pores in the membranes are not absolute since the sizes of the pores in the skin of the membrane vary. It is important therefore during the manufacture of these membranes that attention be given to control not only the average membrane pore sizes but to ensure narrow pore-size distributions.

The mechanism of retention of ultrafiltration membranes differs from that of sand-filtration in that the membrane is a surface filter and entrapment of retained species in the bulk of the membrane does not occur as with sand filters. For this reason there is no break-through of retained species as commonly occurs with depth filters.

By definition, ultrafiltration membranes cannot desalinate water. However, the membranes can reduce the concentration of hydrous species such as ferric and aluminium substantially. If a secondary layer of retained species build-up on the membrane surface (concentration polarization or gel-layer), the membranes can also reduce slightly the concentration of divalent species such as sulphate, magnesium and calcium.

B. Nanofiltration

Nanofiltration is an intermediate desalination operation. It is also referred to as a water softening operation as it retains divalent species to a far greater degree than it does monovalent species such as sodium and chlorides. The retention performance of these membrane is not based on size exclusion, but rather on the principle of solution diffusion,

that is, retention is based on the different rates of diffusion of the species through the membrane.

Nanofiltration membranes are capable of retaining organic species of very low molecular mass and as such the process is excellent for colour removal. The membranes are more dense than ultrafiltration membranes, so that they have greater capabilities for the removal of microorganisms.

However, the operating pressure of these membranes is an order of magnitude higher than that of ultrafiltration; typically from 1 to 1,5MPa.

III. MEMBRANE AND MODULE CONFIGURATIONS

1. SUPPORTED TUBULAR MEMBRANES

Tubular membranes have the advantage of an open-flow channel so that they offer the possibility of operation on less than clean water. Similarly these membranes offer the possibility of very high water recovery rates as they can tolerate a higher concentration of suspended solids in the feedwater.

Tubular membranes are available in diameters that range typically from 8 to 25mm. They are cast on the inside of a filter tube welded from a non-woven spun-bonded polyester or polypropylene fabric. The narrow-bore 8mm diameter membranes are self-supporting at lower operating pressures (typically 2 to 3 bar). Although these pressures are adequate for operation of an ultrafiltration process, they are much below the operating pressure for nanofiltration. For this reason the tubular nanofiltration membranes must be housed in perforated steel tubes, which act as a pressure support system. The membranes are normally housed in a tube-in-shell arrangement. In one design the membranes are sealed to the perforated stainless steel support tubes at either end with a rubber grommet, and 18 individual tubes in a module are manifolded into a series arrangement by means of a specially designed end-cap bolted onto the tubesheet.

Plastic disks are used in another less expensive tubular module design. The injection-moulded plastic disks have 19 holes that form tubular passages when the disks are lined up correctly. The membranes are inserted into these bodies which in turn are inserted into a metal shroud. In a module arrangement in which the tubular membranes are connected

in series, the tubesheets are formed by inserting plastic return bends into the open ends of the membranes, and encasing the end-assembly in epoxy.

2. UNSUPPORTED CAPILLARY MEMBRANES

Capillary membranes have advantages in addition to those offered by the tubular configuration. They are self-supporting because of their narrow diameters (typically 0.7 to 2.5mm), and they may be pressurized internally or externally. The internally skinned membranes are operated from the lumen side, that is, they are internally pressurized and filtrate permeates from the inside to the outside. However, they may also be operated in the reverse direction (i.e. outside to inside) without collapsing. This may be used to introduce a back-flush by which the membrane surface may be cleansed of foulant deposits either by reverse flow of product water.

The use of air as a backflush medium for ultrafiltration membranes depend on the MMCO of the membrane. Excessively high air pressures would be required to backflush membranes with small pores to achieve convective transport of air because of the capillary forces due to the high surface tension of the water filling the pores. However, with membranes of larger pore diameters, typically >50nm, air may be considered as a means for backflushing the membrane by convective air transport.

Capillary membranes must also be incorporated in a membrane-holding device or module, before they can be put to any practical use. Two axial-flow membrane module prototypes were used during the study. The modules were of tube-in-shell cartridge-type design which proved very simple to scale up to larger-sized units. It was important, however, that the cost per cartridge be kept as low as possible, without reducing the efficiency of either the process or the design.

The idea of a cartridge module originated at the time when modules were devised for incorporation in the cross-face flow manifolds then under development in another WRC-funded programme. The simplest and least expensive manifold for the cartridge type modules comprised a row of uPVC T-pieces with their straight ends solvent-welded together. The modules, which were fitted with two O-ring grooves on either end (Figure 2), were then simply push-fitted inside the side-branches of the T-pieces where the O-rings provided a seal against the inside of the side-branch to prevent process fluid leakage.

Hennenman and Theunissen (Vorster vd Westhuizen and Partners). A map of the area based on the expanded boundaries is shown on Map C3.

The population within the area is estimated as follows:

Urban Foundation boundaries	468 000
Expanded boundaries	520 000

It is estimated that the population is growing at a rate of 3,5% per annum, which is faster than the urban average for the country of 3,2%.

The goldfields area is essentially a grouping of medium sized towns. Using the narrower definition of the area these are: Welkom/Thabong, Virginia/Meloding, Odendaalsrust/Kutlwanong and Allanridge. Hennenman/Phomolong and Theunissen/Masilo are included in the expanded area. By far the largest of all these towns is Welkom/Thabong which has a population of 344 000, two thirds of the total.

c) Orange Free State towns

The remainder of the Orange Free State consists of a multitude of smaller towns spaced at fairly uniform distances. There are 136 local authorities in the non-metropolitan part of the OFS. If the black local authorities are grouped with their adjacent "white" local authorities,

The across-face manifold (See Figure 3) was designed specifically to allow the feed-water to pass over the faces of the capillary membranes. The reason for this was not only for simplicity, but also to provide a means for counteracting the tendency for particulate material to accumulate at the module entrance, bridge, and eventually block the capillary lumen. As can be seen from the figure, the cartridge ends are placed in the manifold in such a way that the feed flow sweeps the faces of the cartridges. Because, under operating pressures the inlet and outlet manifolds would tend to move apart, the manifolds were braced so as to prevent this.

Across-face flow can be achieved by switching an inlet manifold recycle pump which circulates the process fluid in the manifold in a closed loop. This centrifugal pump can be operated continuously or be operated by means of a time switch.

In another embodiment of the cartridge-type design, the cartridges were fitted with removable flanges on either side. The modules could be fabricated from welded stainless steel tube, which is reasonably inexpensive, or uPVC tube. The photograph in Figure 4 shows the flanged-type module. Figure 5 shows that the stainless steel flange (which is an expensive part of the module) can be removed once the flange is slid backwards and the exposed steel circlip retainer ring (an O-ring may also be used) removed.

Both module designs were used in the experiments at Uitenhage. The module shown in Figure 3 was prepared from a 600mm-long transparent uPVC tube with an outside diameter of 40mm. A total of 119 membrane fibres with inside diameters of 1.07mm were packed into each of these modules. Each module had a membrane surface area of 0.2 m^2. O-ring grooves were machined into the tubesheet and four of the modules were mounted into the 40mm T-piece manifold of the UF test rig, giving a total membrane area of 0.8m^2.

The second flange-mounted module prototype had a surface area of 1m^2, housed within a 1,2m-long 50mm outer diameter stainless steel shroud. The membranes were internally skinned and a module contained 270 fibres with inside diameters of 1.2mm . The membranes had an instantaneous burst pressure of 2.3MPa. The modules were flange-connected.

ules

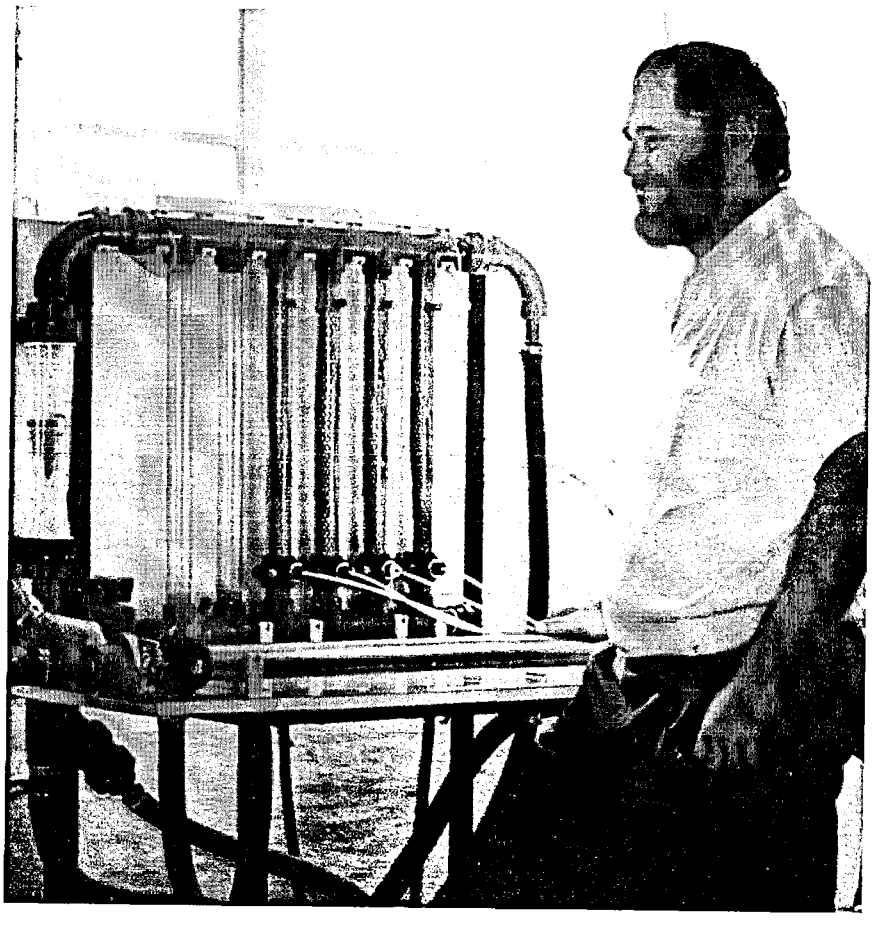

Figure 3: Across-face manifold for 40mm modules

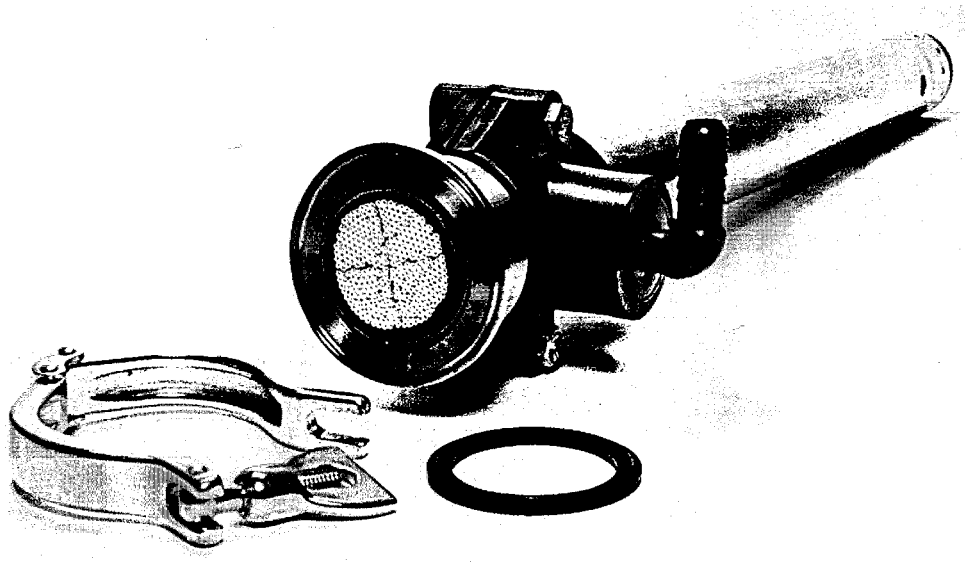

Figure 4: Photograph of a 50mm axial-flow membrane cartridge with flanged connector design.

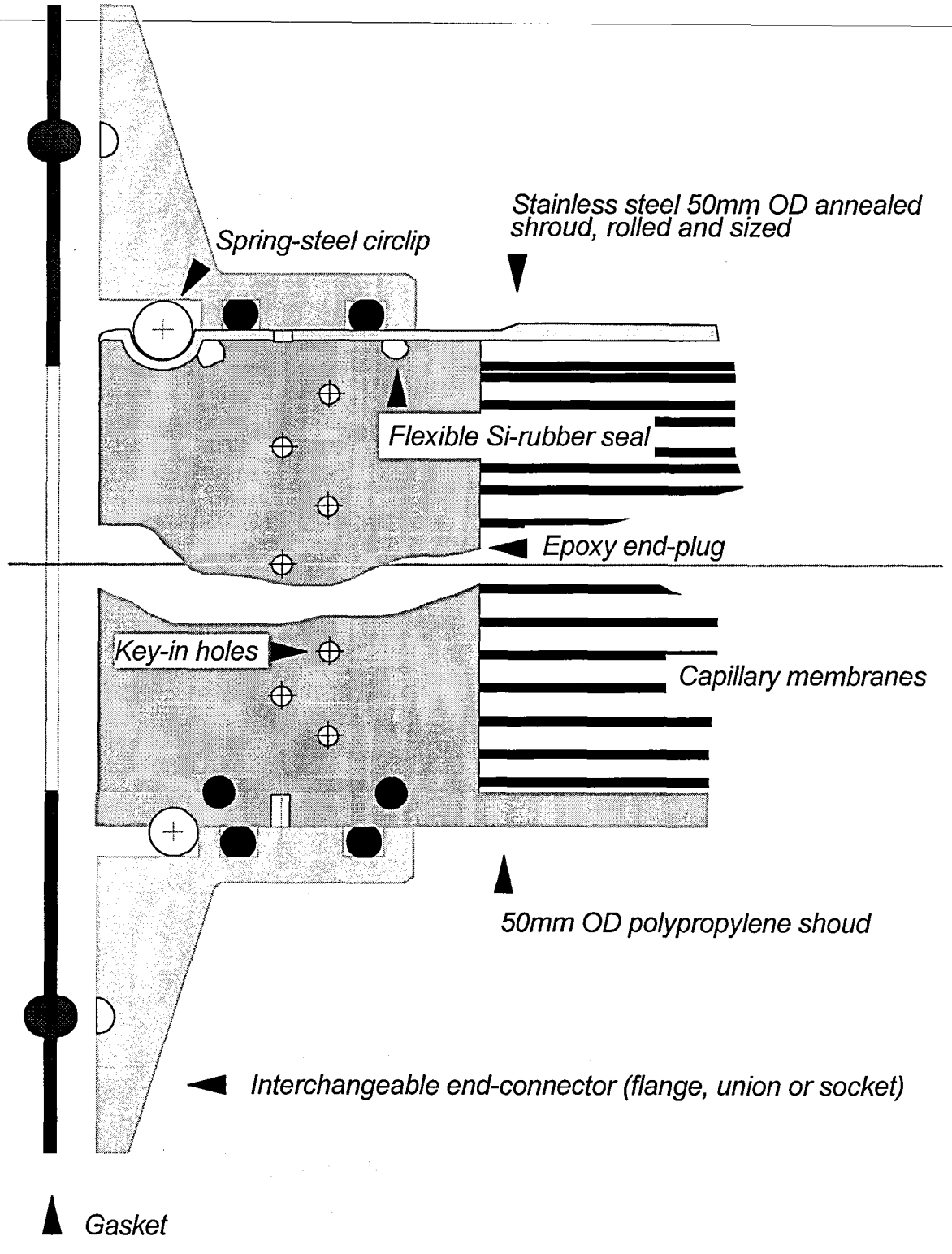

Figure 5: Schematic diagram of a 50mm flanged cartridge module

3. MEMBRANE PRODUCTION

A. Tubular nanofiltration membrane production

Pressure-driven membrane separation processes, as we know them today, owe their development to the discovery, early in the 1960s, of a technique for producing asymmetric reverse osmosis (RO) membrane films from cellulose acetate. The technique can also be used to produce non-desalting microfiltration membranes from poly(vinylidene fluoride) or poly(ether imide), ultrafiltration membranes from polysulphones or polyacrylates, or nanofiltration membranes from cellulose acetate. Nanofiltration membranes are loose, open RO membranes which, at medium to low operating pressures, discriminate in their separation of mono- and divalent inorganic species. These membranes also retain organic fractions that would otherwise pass freely through low-molecular-mass cut-off UF membranes. Nanofiltration is an economically and technically viable process for water-softening and/or removing colour from surface or process-effluent streams. In this section some aspects of the development of a low-operating-pressure tubular cellulose acetate nanofiltration membrane will be discussed.

(i) Phase inversion

Skinned (asymmetric) or unskinned (symmetric) membranes, are generally produced by phase inversion. In this process a homogeneous polymer solution is transformed into two liquid phases, one a polymer-rich phase and the other a solvent-rich or polymer-poor phase. The polymer-rich phase coagulates to form the membrane bulk, whereas the polymer-poor phase forms the matrix of interconnecting pores and passages within the skin and bulk structure of the membrane. Phase-inversion membranes can be formed from any polymer mixture which forms a homogeneous solution under certain conditions of composition and temperature, but which separates into two phases at other compositions and temperatures, provided that:

- ❑ the two phases that form during phase inversion are both continuous; and
- ❑ solvents, non-solvents and polymer additives that are used in formulations are soluble in the non-solvent medium used as coagulant.

In the wet-phase inversion process, water is the most commonly used coagulant for effecting this change in phase.

(ii) Membrane fabrication

Any factor that has an effect on the kinetics or thermodynamics of the inversion process will affect the morphology and the transport performance of the membrane. The following are some of the important factors that must be considered in the design of a membrane production protocol:

- ❑ nature of true solvents, latent and non-solvents used;
- ❑ polymer and inorganic additives used in the casting formulation;
- ❑ the membrane-forming polymer material(s);
- ❑ relative concentrations of the various components of the casting formulation; and
- ❑ viscosity and temperature of the membrane-forming dope.

Other factors include:

- ❑ temperatures of the extrudate, environment and the coagulant;
- ❑ air-gap, or time of membrane exposure between point of film extrusion and coagulation;
- ❑ inorganic and solvent additives and concentration-levels in the coagulation bath; and
- ❑ rate of membrane production.

(iii) 2-Level factorial experiments

A broad field of statistics is devoted to the planning of experiments. One of these experimental designs is the 2-level factorial experiment [1]. This experimental design involving n factors (i.e. the 2^n factorial), requires 2^n combinations of two levels for each of the n factors (i.e., 2^n experiments or treatment combinations in total). In a full factorial design, in effect, each of the n factors is considered at both a low level and a high level, and the variable considered is transformed to a minus for the low level or a plus for the high level (See the layout given in Table 6). These designs offer an ideal means by an experimental region can be explored to gain maximum information with the least amount of experimentation, and they have formed the basis of the approach to establish fabrication protocols by which a high-flux 40% NaCl-retention nanofiltration membrane can be produced.

(iv) Membrane formulation

A large number of variables need careful control during the fabrication of membranes to ensure replication and consistency in the performance of the membranes produced. On the other hand, by changing the level of factors such as the casting-solution formulation, membrane-annealing temperature and time, and even ambient conditions such as humidity and temperature etc., the performance of such a membrane-system can be adjusted to different values. However, membrane flux is an important economic consideration, and much effort is expended to increase membrane flux performance. Earlier work indicated that the retention performance of CA membranes can be closely controlled by adjusting the level of only four factors (only, however, if the levels of a number of other factors are kept constant). The factors that were considered in this study were:

- ❑ polymer concentration in the casting-solution formulation;
- ❑ acetone (solvent)-to-formamide (non-solvent) ratio in the formulation;
- ❑ concentration of a non-solvent modifier (here expressed as percentage of the solvent, acetone fraction in the formulation); and the
- ❑ membrane annealing temperature. The four-component formulation is completely described by the three factors that relate to the casting solution.

(v) Experimental approach to membrane development

The following experimental approach was used to determine the fabrication protocols for a productive 40% NaCl-retention nanofiltration membrane:

- ❑ explore the experimental region in the above four factors by means of two-level factorial experiment(s);
- ❑ model the flux and retention response by multiple linear regression to fit a generalized Taylor series model:

$$y^* = \beta^O + \sum_{i=1}^{n} \beta^i x_i + \sum_{j=i+1}^{n} \sum_{i=1}^{n} \beta^{ij} x_i x_j + \ldots$$

- ❑ conduct experiments at the centre-point of the factorial experiment to determine how well the real response surfaces are presented by the planar Taylor series model (The experimental design used did not provide the necessary degrees of freedom to include coefficients of higher order); and
- ❑ investigate the flux and retention regression equations numerically to obtain those fabrication conditions that will ensure the production of a membrane with

optimum flux at the specified NaCl retention of 40%.

(vi) Membrane evaluation

The membranes were evaluated against 2g/l NaCl in a closed-loop test system the temperature of which was controlled at 20±0,1°C. The operating pressure was maintained at 1MPa, the linear cross-flow velocity in the 13mm tubular membrane at 1m/s and the recovery was kept at zero percent. The membranes were contained in 500mm-long test cells. The performance of the membranes was judged by water-flux, expressed as litres per square metre membrane area per hour (Lmh), and percentage conductivity retention of the NaCl after 4h of operation. The performance of CA membranes can be compared by the log relationship of their pure-water permeability and salt permeability coefficients. The basic equations for transport through an RO membrane are:

water flux: $F_1 = A\left[\Delta P - \left(\pi_W - \pi_p\right)\right]$

and the salt flux: $F_2 = B\left[C_W - C_p\right]$

ΔP	pressure difference across the membrane
$\Delta\pi$	osmotic pressure difference across the membrane
ΔC	concentration difference across the membrane
A	pure-water permeability coefficient (A-value)
B	salt permeability coefficient (B-value)
π	osmotic pressure
C_W	NaCl concentration at upstream membrane interface
C_p	NaCl concentration at downstream membrane interface

As the desalinated water product permeates through the membrane there is an increase in solute concentration at the membrane-brine interface. The magnitude of this concentration increase or polarization at the membrane interface depends on the relative rate of convective flow towards the interface, diffusive flow away from the interface and linear rate of flow across the membrane. The relationships given earlier have been suitably modified to calculate the A-values and B-values of tubular cellulose acetate membranes subject to concentration polarization, and under conditions of turbulent flow. These relations were used in the calculation of permeability coefficients shown later [2,3].

(vii) Numerical optimization

Numerical optimization was achieved by means of a software package, Eureka, coded for use on a personal computer. This package is powerful enough to solve equations with four variables simultaneously and was able to converge to an answer within 3 min on a 386SX (20MHz) machine. The numerical optimization procedure followed was to maximize:

flux:: $f^f(x_1, x_2, x_3, x_4)$ subject to the inequality constraints:

retention: $f^r(x_1, x_2, x_3, x_4) \rangle 40$

and $-1 \leq x_i \leq +1, \ (i = 1...4)$

(viii) Results and discussion

Thermal treatment in hot water is a well-known procedure used to increase the salt retention by cellulose acetate membranes. However, the densification of the skin-structure caused by the annealing step has the reverse effect on the water transport rate of the membrane. Figure 6 clearly shows the effect that annealing temperature has on membrane flux and retention performance.

An important aspect of this study was to determine whether any net gain in flux performance could be achieved if porosity-modifying additives were used to offset the reduction in flux that resulted from annealing. For this purpose, very small quantities of the non-solvents water, glycerol and formic acid were added to the formulation. Table 6 shows the factor levels studied for the different cases as well as the results of the full 2^4 factorial experiment in which formic acid featured as a non-solvent additive to the solvent used, namely acetone.

The flux and retention responses obtained from the 2^4 factorial experiment where formic acid featured as additive were regressed as follows:

Flux: $F = 40{,}874 - 3{,}396x_1 - 5{,}071x_2 - 9{,}776x_3 - 9{,}577x_4 + 1{,}547x_1x_2 - 1{,}671x_1x_3 + 1{,}103x_1x_4 + 5{,}454x_2x_3 + 0{,}0996x_2x_4 + 0{,}658x_3x_4 + 0{,}397x_1x_2x_3 - 2{,}192x_1x_2x_4 + 3{,}093x_1x_3x_4 + 0{,}156x_2x_3x_4 - 1{,}727x_1x_2x_3x_4$

Retention: $R = 26{,}988 + 3{,}661x_1 + 1{,}573x_2 + 9{,}420x_3 + 4{,}134x_4 - 0{,}491x_1x_2 + 2{,}281x_1x_3 - 1{,}565x_1x_4 - 2{,}878x_2x_3 - 0{,}529x_2x_4 + 1{,}564x_3x_4 - 0{,}439x_1x_2x_3 + 2{,}250x_1x_2x_4 - 2{,}453x_1x_3x_4 - 1{,}176x_2x_3x_4 + 1{,}600x_1x_2x_3x_4$

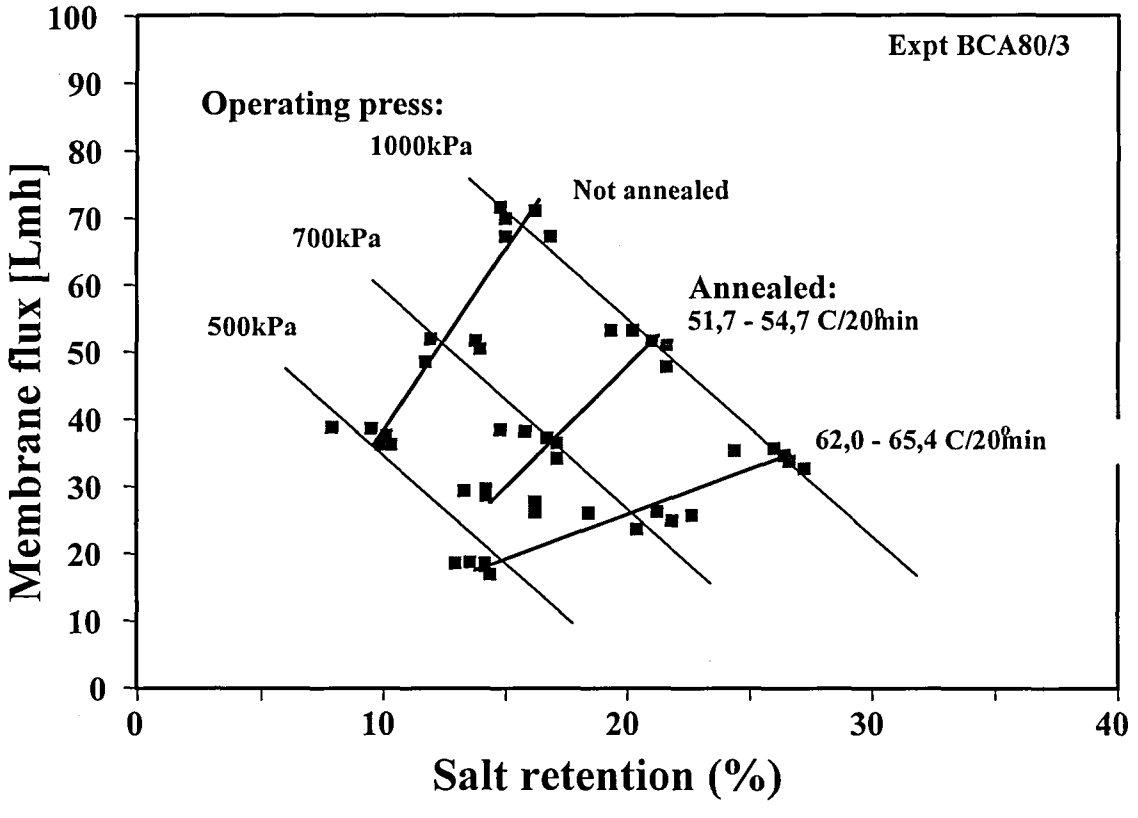

Figure 6: Flux and salt retention performance of CA membranes at different operating pressures and annealing temperatures

Table 6: Factor levels for 2^4 factorial and the flux and retention response for the treatment combinations of the full 2^4 factorial experiment

Factors		Variable level		
		Low	Centre	High
		-1	0	1
A	Cellulose acetate concentration (mm%)	23	23.45	23.9
B	Acetone/formamide mass ratio	1.4	1.45	1.5
C	Formic acid concentration in acetone (mm%)	0	0.75	1.5
D	Annealing temperature (°C)	75	78.5	82

Treatment	Variables				Flux	Retention
combinations	x_1	x_2	x_3	x_4	(Lmh)	(%)
I	-1	-1	-1	-1	73.6	10
a	1	-1	-1	-1	70.9	12.4
b	-1	1	-1	-1	47.6	19
ab	1	1	-1	-1	51.4	18.6
c	-1	-1	1	-1	44.1	26.9
ac	1	-1	1	-1	25.7	45.1
bc	-1	1	1	-1	42.7	25.9
abc	1	1	1	-1	35.9	36.3
d	-1	-1	-1	1	54.5	13.4
ad	1	-1	-1	1	45.7	16.7
bd	-1	1	-1	1	33.8	22.4
abd	1	1	-1	1	27.7	28.1
cd	-1	-1	1	1	19.5	46.1
acd	1	-1	1	1	21.8	44.1
bcd	-1	1	1	1	26.6	34.3
abcd	1	1	1	1	20.9	43.9

These regression equations illustrate the inverse relationship (opposite signs of the regression coefficients) between retention and flux, that is, an increase in salt retention is generally associated with a reduction in the permeate volume flow. With the assistance of the Eureka code, the equations were used to formulate numerically a 40% retention membrane with optimal flux performance. There was close correlation between predicted values and experimental results.

The pure-water-permeability and salt-permeability coefficients of membranes produced from formulations containing formic acid, glycerol and non-solvent modifiers are compared in Figure 7. From these, formic acid appears to be an attractive additive with a pronounced effect on salt retention. Regression lines drawn through the experimental and numerically generated membrane performances (Figure 8), give a clear indication that membrane performances can be further improved by formulating the membrane fabrication protocols numerically. Figure 9 shows the salt-retention performance of the formulated membrane within the experimental region demarcated in Table 6. Again there was close correlation between calculated values and experimental results.

(ix) Conclusions

2-Level factorial experiments offer a simple way to multiple linear regression because of the orthogonality of the experimental designs. When they are used in conjunction with numerical techniques, formulation of an intricate membrane system to achieve maximum flux performance for a given level of salt retention is simplified.

B. Ultrafiltration capillary membrane production

Capillary membranes are spun by extruding a membrane-forming solution through an annular (tube-within-tube) die (See Figure 10). This die contains an exit ring-opening for the casting solution and a centre opening for metering the core- or lumen-forming medium. When the wet-jet technique is used, a non-solvent coagulant is metered into the lumen of the nascent membrane. This fluid not only keeps the lumen from collapsing, but also participates in the coagulation process which leads to the eventual formation of the membrane. The outside of the membrane is also contacted with a non-solvent to enable the polymer to complete the membrane-formation process.

By adjusting the casting-solution formulation and coagulation protocols, membranes can be produced which:

- ❑ are internally or externally skinned,
- ❑ have dense, honeycomb or tear-shaped macrovoid substructure morphologies, and
- ❑ are ultrafilters or microfilters.

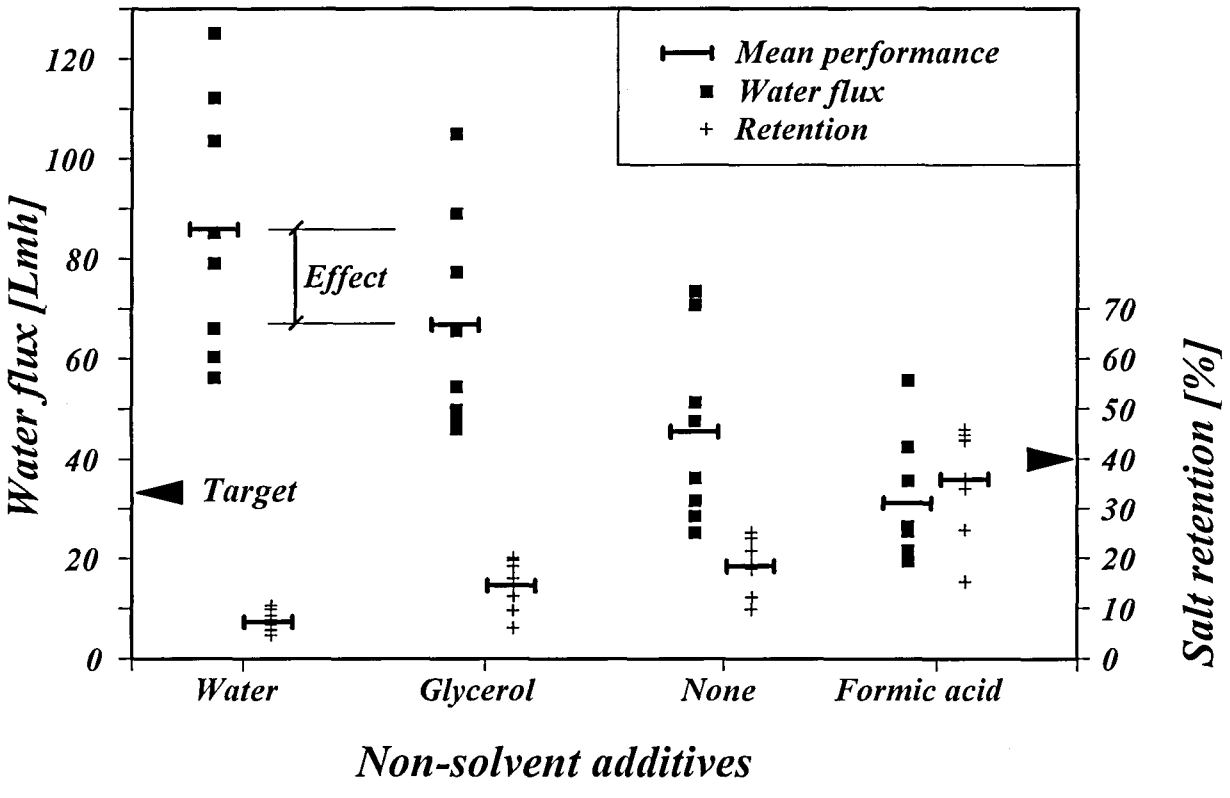

Figure 7: Effect of small quantity non-solvent additions on membrane performance

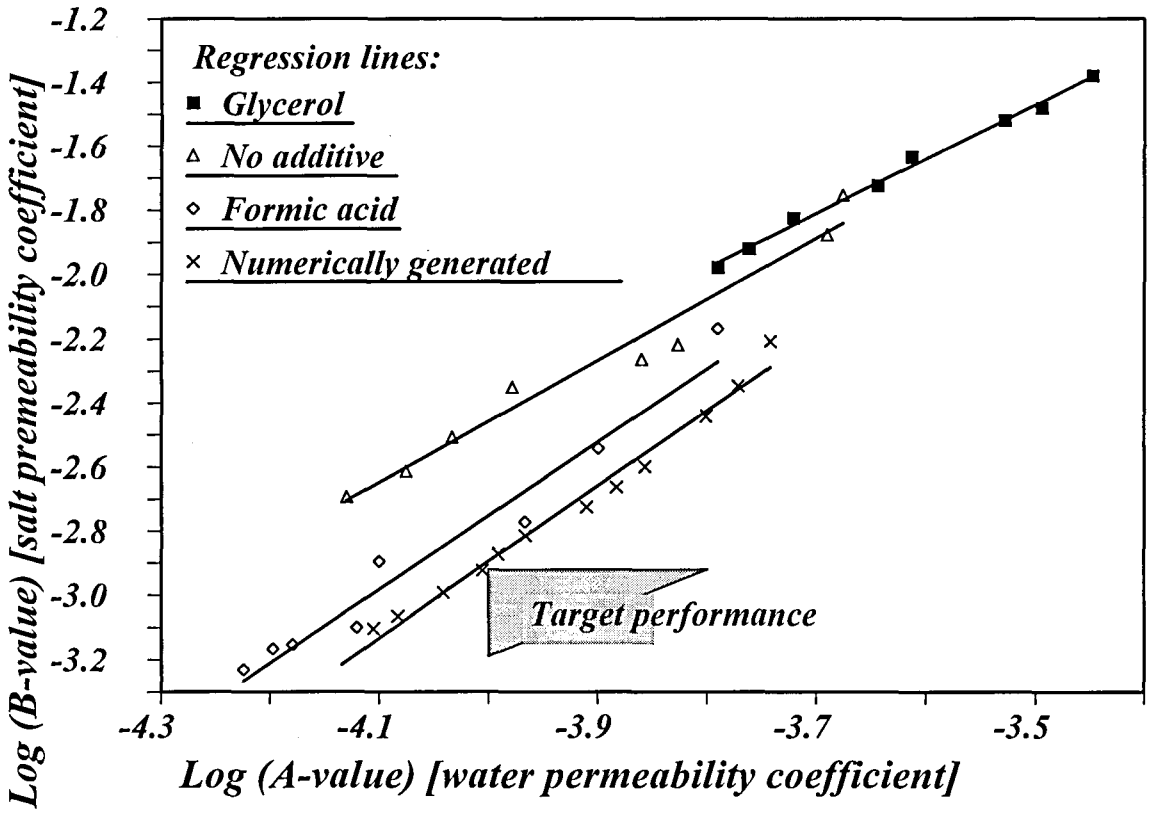

Figure 8: Comparison of membrane performance for various casting solution non-solvent additives

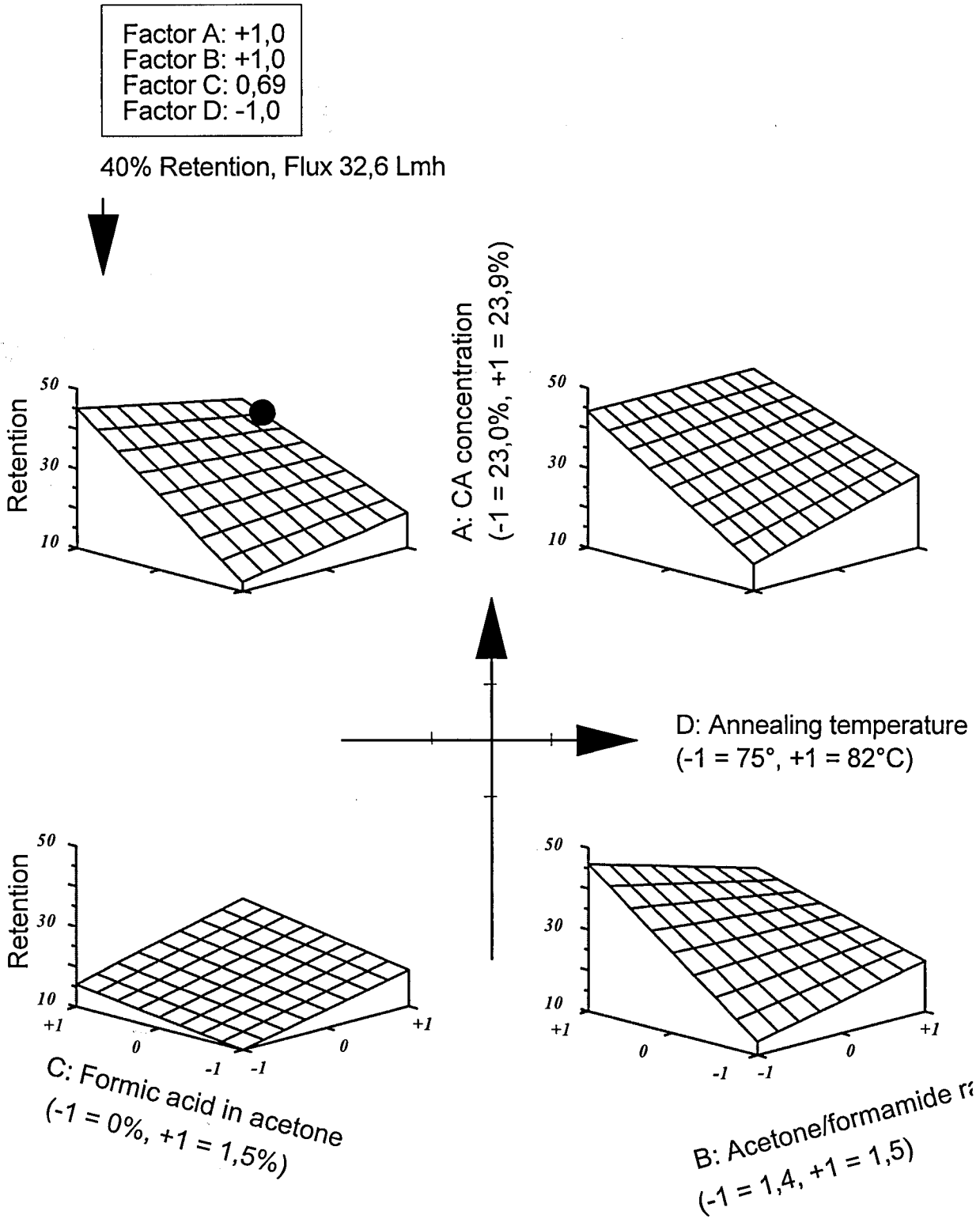

Figure 9: The retention response surface in the experimental window and retention performance of an optimum formulated membrane

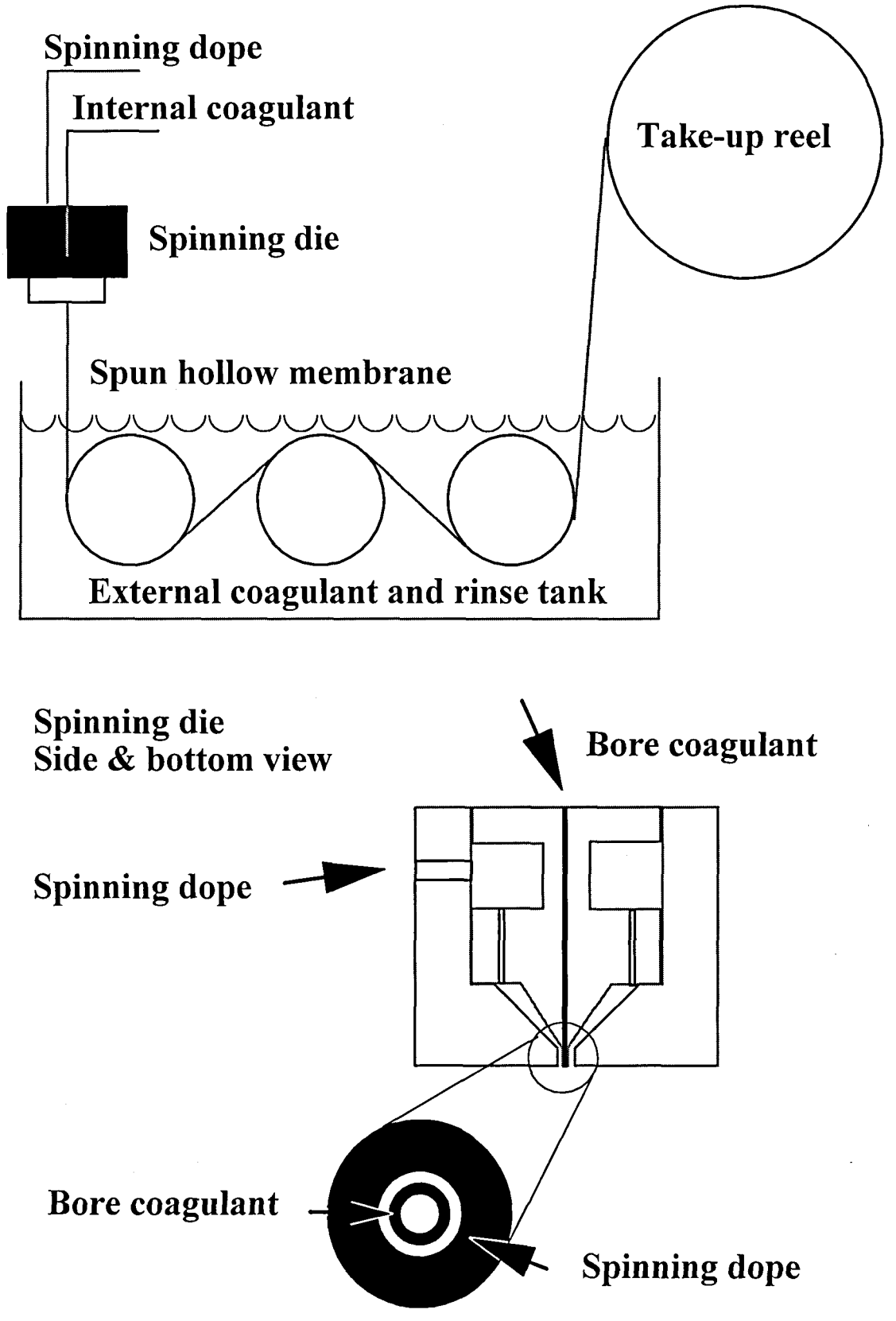

Figure 10: Annular spinning die for capillary membranes

If the membrane is cast into a strong non-solvent, the membrane will have a noticeable skin on the outside. If a membrane is cast into a weak non-solvent or a weak solvent, an imperfect external skin results. Likewise the core-fluid can be of similar composition, in which case a skin may or may not result on the inside.

The extruded membrane is drawn mechanically away from the spinneret. If a weak non-solvent or weak non-solvent mixture is used as the core coagulant, the viscosity of the internal wall remains relatively low and the membrane can be drawn to sizes a magnitude smaller than that extruded. However, if a strong non-solvent is used as core coagulant, the skin reaches maximum viscosity almost immediately and drawing at this stage will have relatively little effect on the membrane diameter.

Figure 11 shows the cross-section of a capillary membrane. The membranes are internally skinned, but have an outside skin of very low definition. When the definition of the external skin-layer is reduced the overall membrane resistance is reduced and the specific flux properties of the membrane are increased.

Code 748 capillary membranes, shown in Figure 11, was used in the Uitenhage experiment. These membranes were cast from a 26% (by mass) solution of poly(ether sulphone) in N-methyl, 2-pyrrolidone (NMP) solution. Additives were used in the formulation to modify the hydrophilicity of the membrane. Pure water at 22°C was used as internal coagulant, whereas an 20% (by mass) aqueous solution of NMP was used as external coagulant.

IV. MEMBRANE PROCESS OPERATION

1. NANOFILTRATION

A. System design

Figure 12 shows the layout of the experimental tubular-membrane-treatment plant. The level of the water in the feed tank was controlled by a ball valve and the system was operated on a feed-and-bleed basis. The recovery ratios were kept low because of the small membrane area and problems with temperature control. A triplex diaphragm pump was initially used as feed pump, but this was replaced after 3000h with a ceramic triplex piston pump. The system was further equipped with pressure gauges, rotameter and pressure control and by-pass control valves.

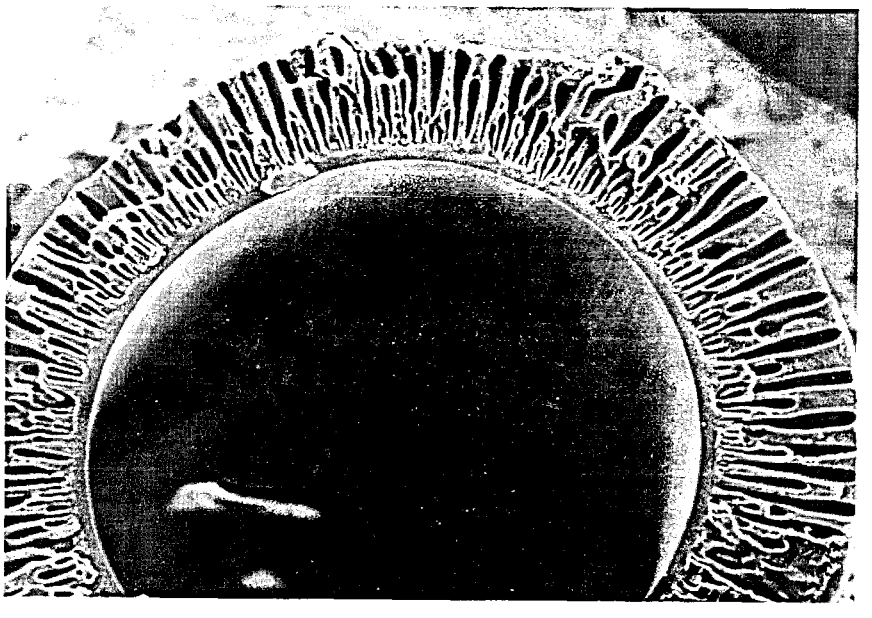

Figure 11: Micrograph of the cross-section of an ultrafiltration capillary membrane

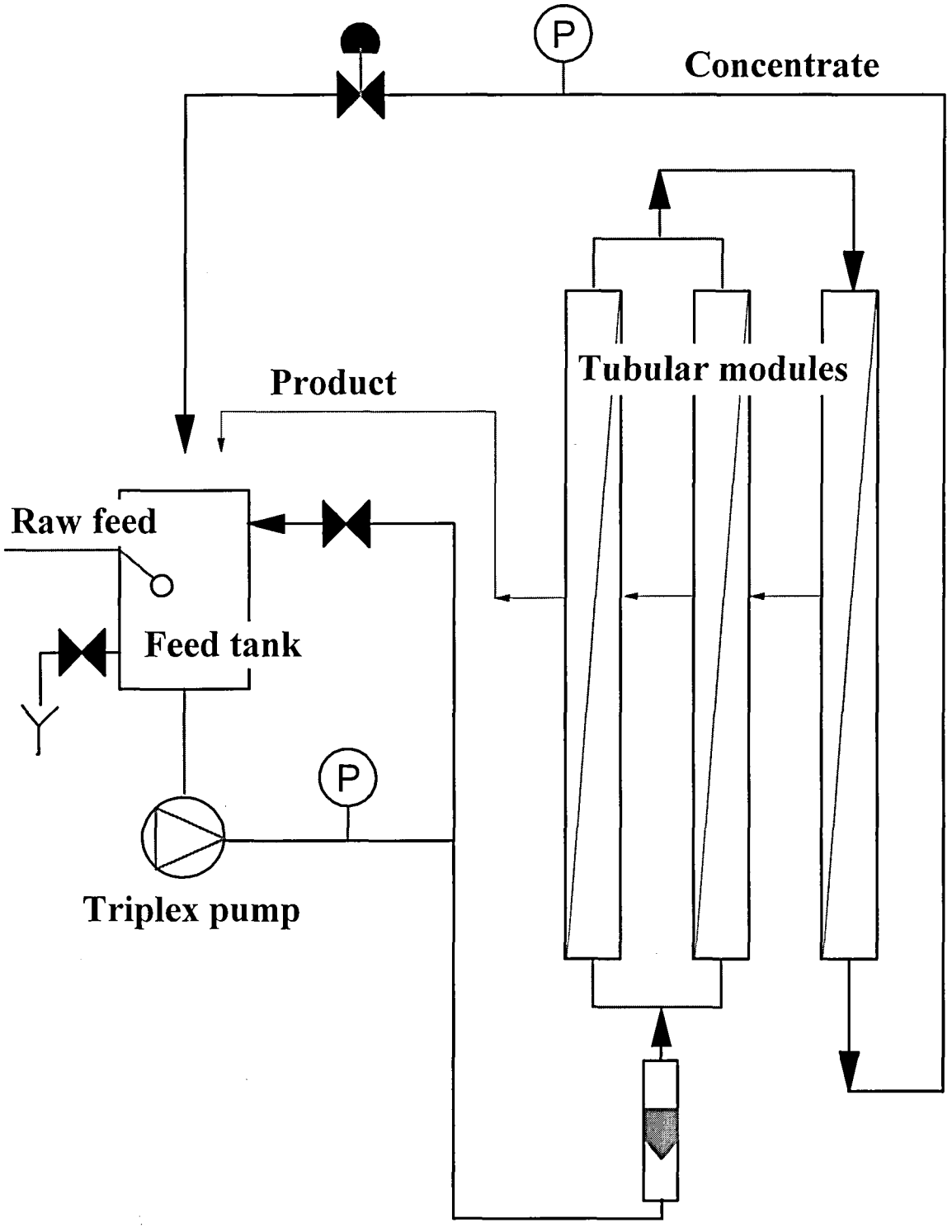

Figure 12: Layout of the nanofiltration system

The system was initially operated with a single module, but two additional modules were later added. The modules were operated in a 2 - 1 cascade, that is, the velocity in the second module was double that of the first two modules.

B. Membrane flux

The nanofiltration plant was operated for a period of more than 14 000h, initially with only one module, at an operating pressure of 1 000kPa. At 9 660h the membranes were replaced and a third module was installed. The flow arrangement was altered to a 2:1 cascade. The system was initially operated at inlet velocities of about 2,5m/s. This was later reduced to 1,5 and 1m/s respectively. Figure 13 shows the linear inlet velocity to the nanofiltration membrane rack (the operating times on all the graphs correspond).

The temperature of the feed water was not controlled and varied considerably during the period of operation, with temperatures below 16°C being observed during the winter months of July, and above 28°C during the summer months of November and December (see Figure 14).

The feed water to the tubular nanofiltration plant was not pretreated in any way and the water was accepted into the plant as such. No chemicals (oxidants or acid) were added to the raw incoming water from the maturation dam to correct the pH, which was, on average, greater than 7 pH units, or to disinfect the water. Operating at such pH levels, however, is not recommended practice for cellulose acetate membranes, but it was the intention to determine the life expectancy of the membranes operating at higher than recommended pH-levels.

The fact that the feed water was not chlorinated was in line with the argument that chlorination encourages aftergrowth: stimulation of microbial activity which metabolizes modified chemical species.

Figure 15 shows the combined flux performance of the membrane plant over the period of operation (the flux values shown were corrected for temperature). The flux values remained fairly stable over the period, declining towards the end when the 2:1 cascade was introduced and the inlet linear velocity was introduced.

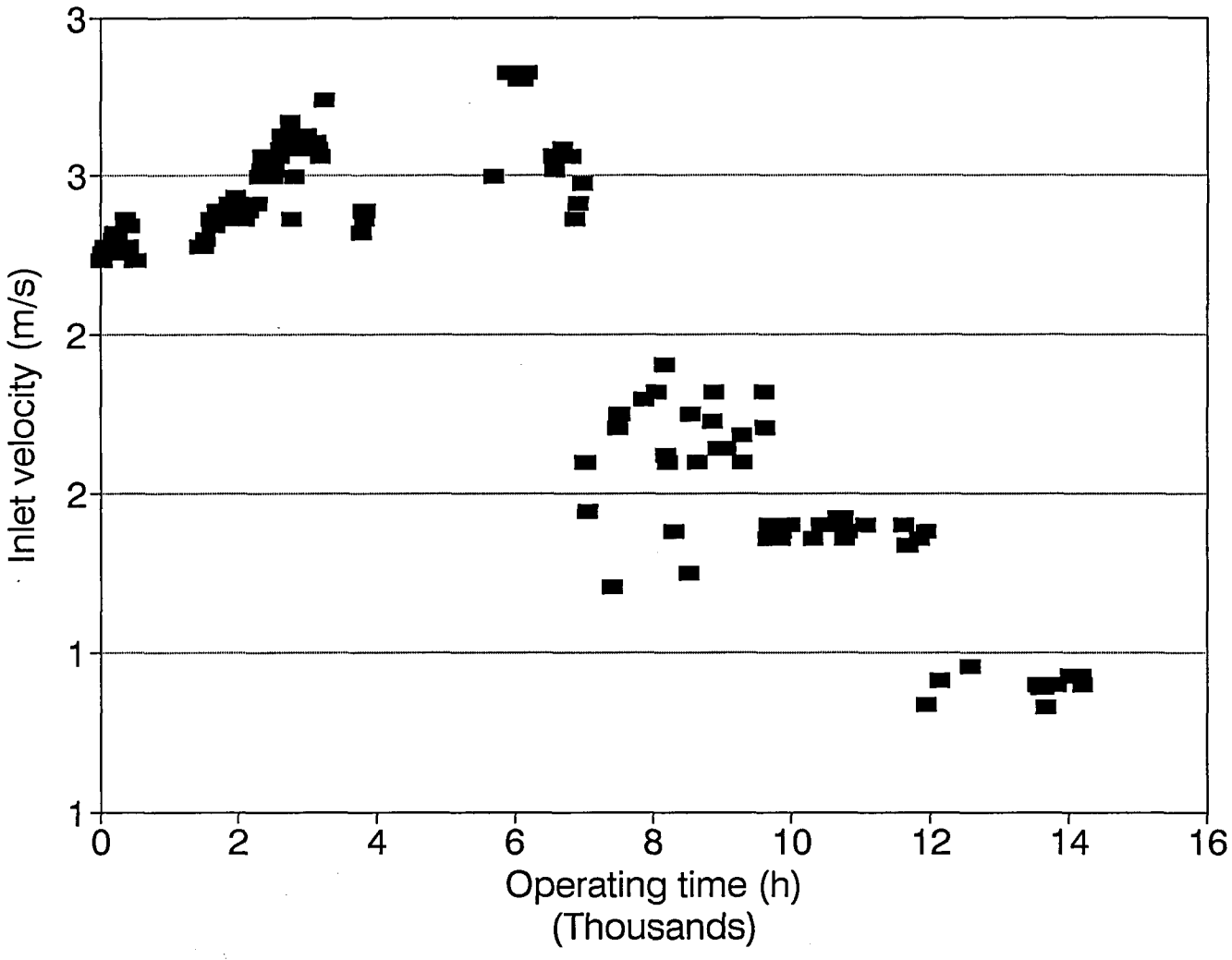

Figure 13: Linear inlet velocity to tubular nanofiltration membranes

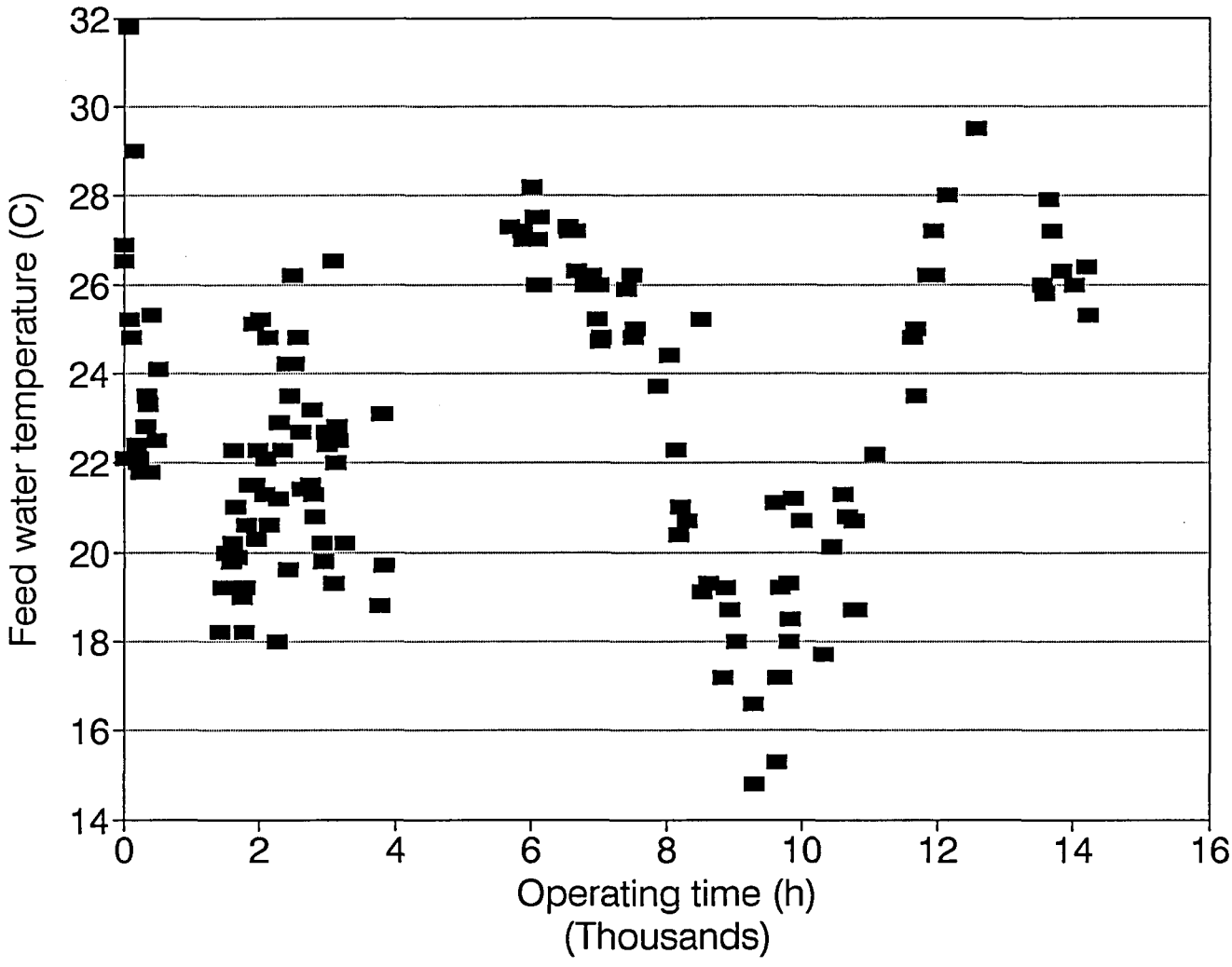

Figure 14: Temperature of raw water feed to tubular nanofiltration membranes

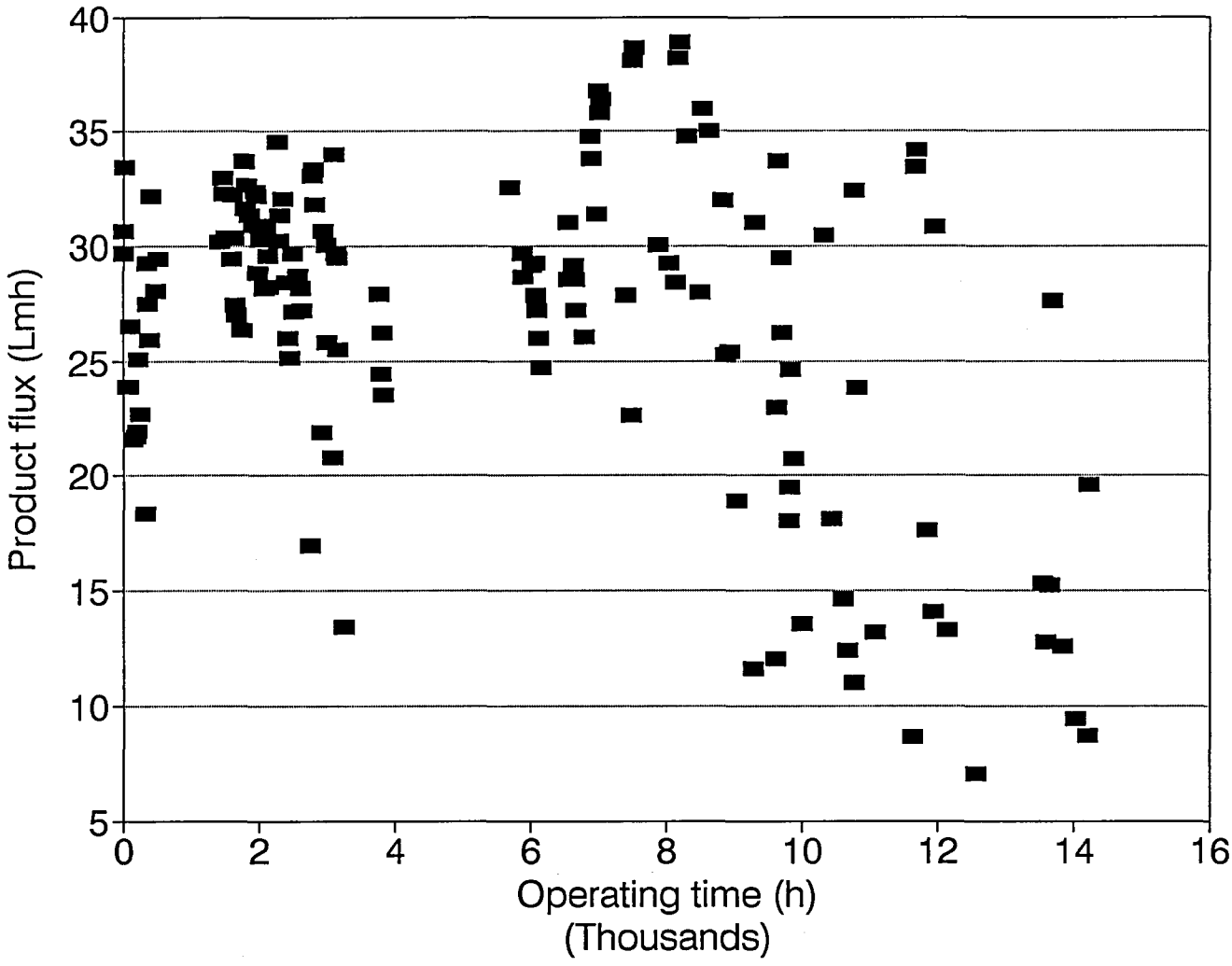

Figure 15: Product flux of tubular nanofiltration membranes

C. Colour removal

The colour-removal performance of the nanofiltration membranes was very high. The colour was measured spectrophotometrically at 455nm (Pt Co). Except for a period between 6 000 and 8 000h operating time when the colour component in the raw water was very low, and the retention capability of the membranes declined, a consistently high retention of colour was attained: on average above 96%. The colour of the product stream was continuously below 10 colour units.

Figures 16 illustrates how the colour content of the maturation pond effluent varied over the period of operation, and Figure 17 shows the colour content of the nanofiltered product water and thus the extent to which the nanofiltration membranes were performing (Figure 18). It must be noted that the sewage-treatment plant treats both domestic and industrial water, and that some of the industries, notably the textile industry, produce a highly coloured effluent. These results underscore the high potential of the nanofiltration process to reduce the organic load in water.

D. COD reduction

The capability of the cellulose acetate nanofiltration membranes to reduce the COD load of the maturation pond effluent is ilustrated in Figure 19. The membranes were consistent in their performance and continuously achieved retentions greater than 70% COD.

These results support the data shown in the earlier graphs and the ability of the nanofiltration membranes to polish water to a very high degree of acceptance.

E. Conductivity reduction

The nanofiltration membranes that were developed were designed to have low NaCl retention. The membranes that were used in the experiments, typically gave NaCl retention values of 30% in the laboratory, with an accompanied laboratory flux of 40LMH (1g/L NaCl feed, 20°C at 1MPa operating pressure).

The conductivity-reduction performance of the membranes was not very high, being on average above 45% (Figure 20). The membranes also showed signs of declining salt retention performance, which could be ascribed to fouling, and also possibly hydrolysis of the

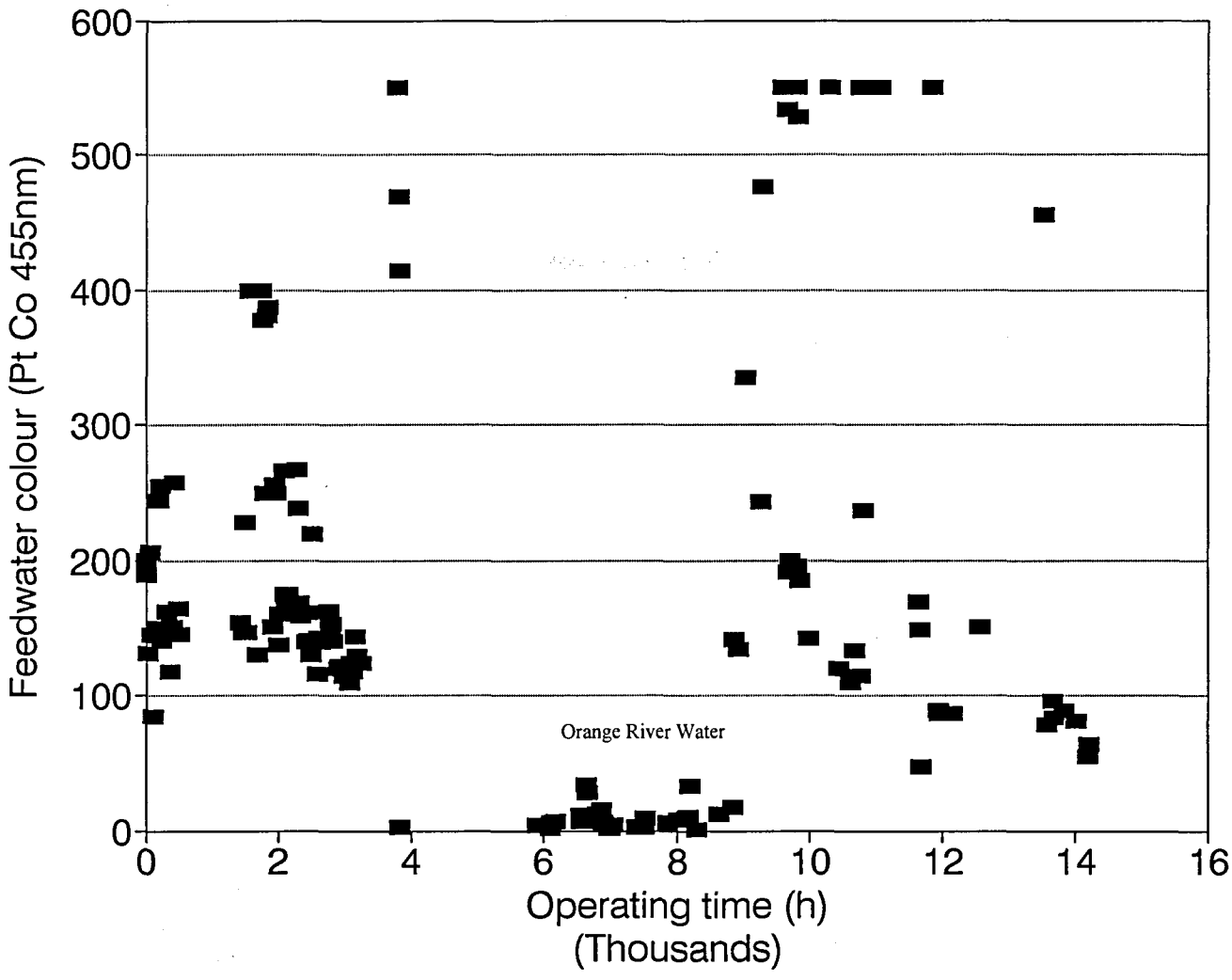

Figure 16: Colour content of maturation pond effluent feed to tubular nanofiltration membranes

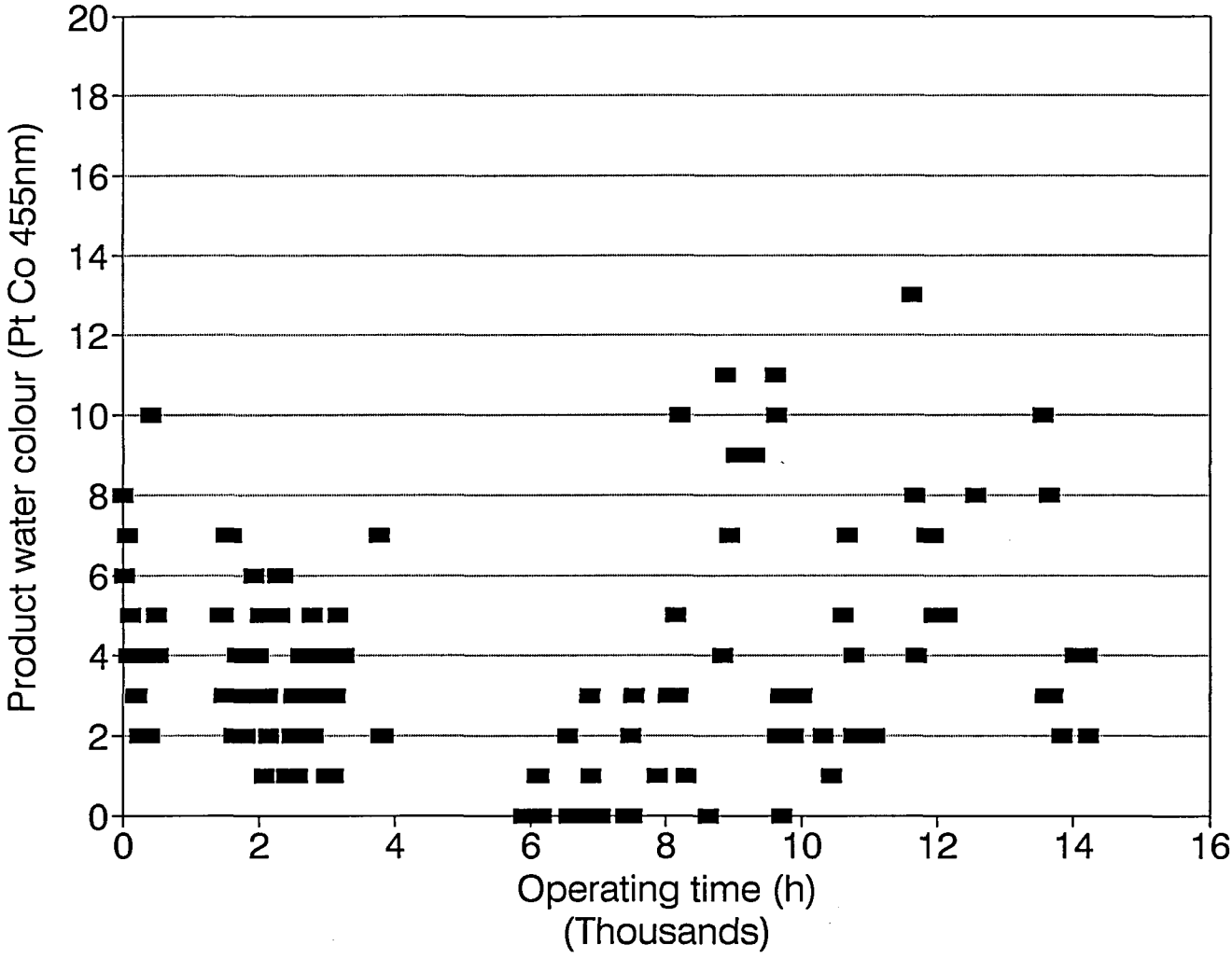

Figure 17: Colour content of nanofiltered product

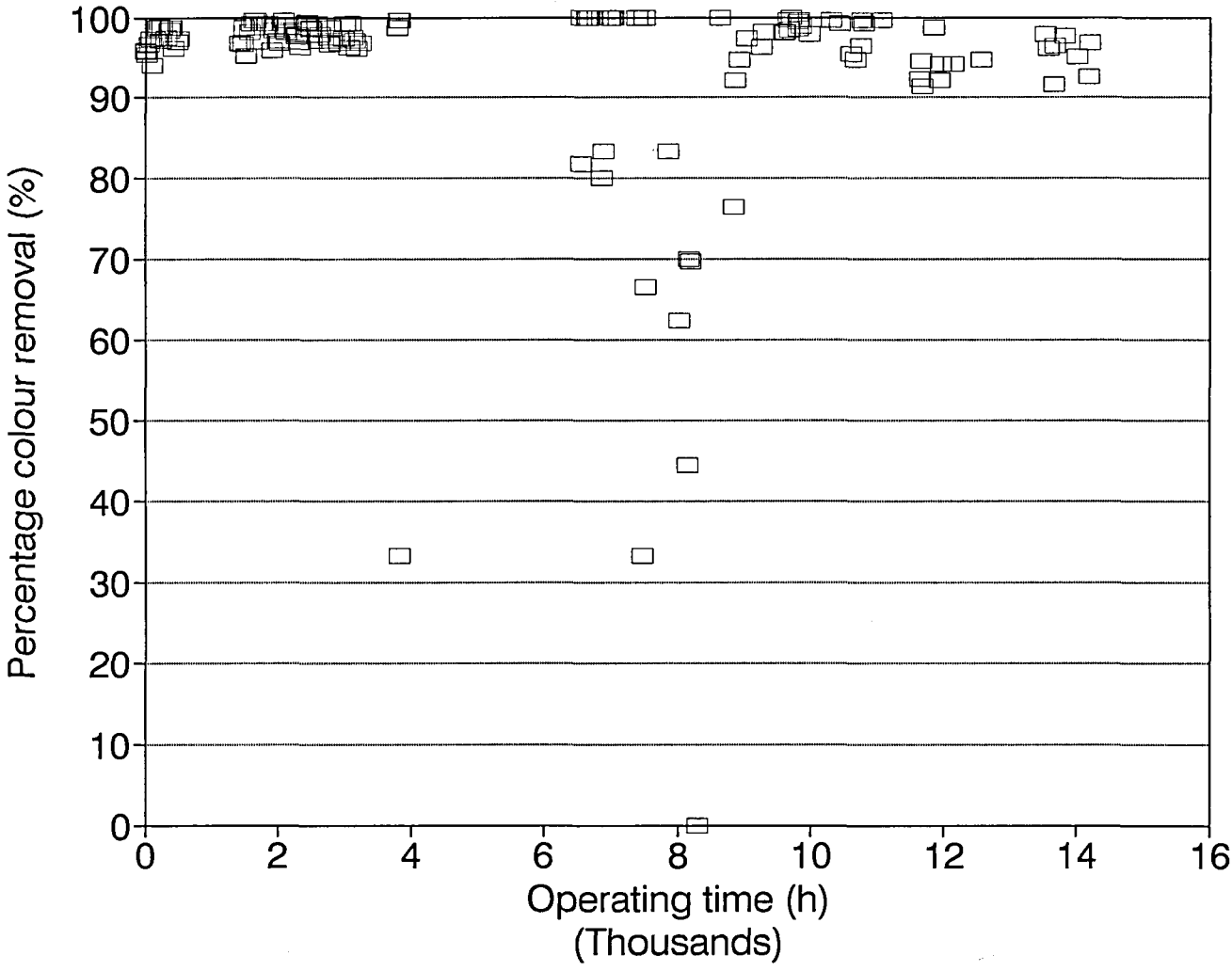

Figure 18: Percentage colour component removal by nanofiltration membranes

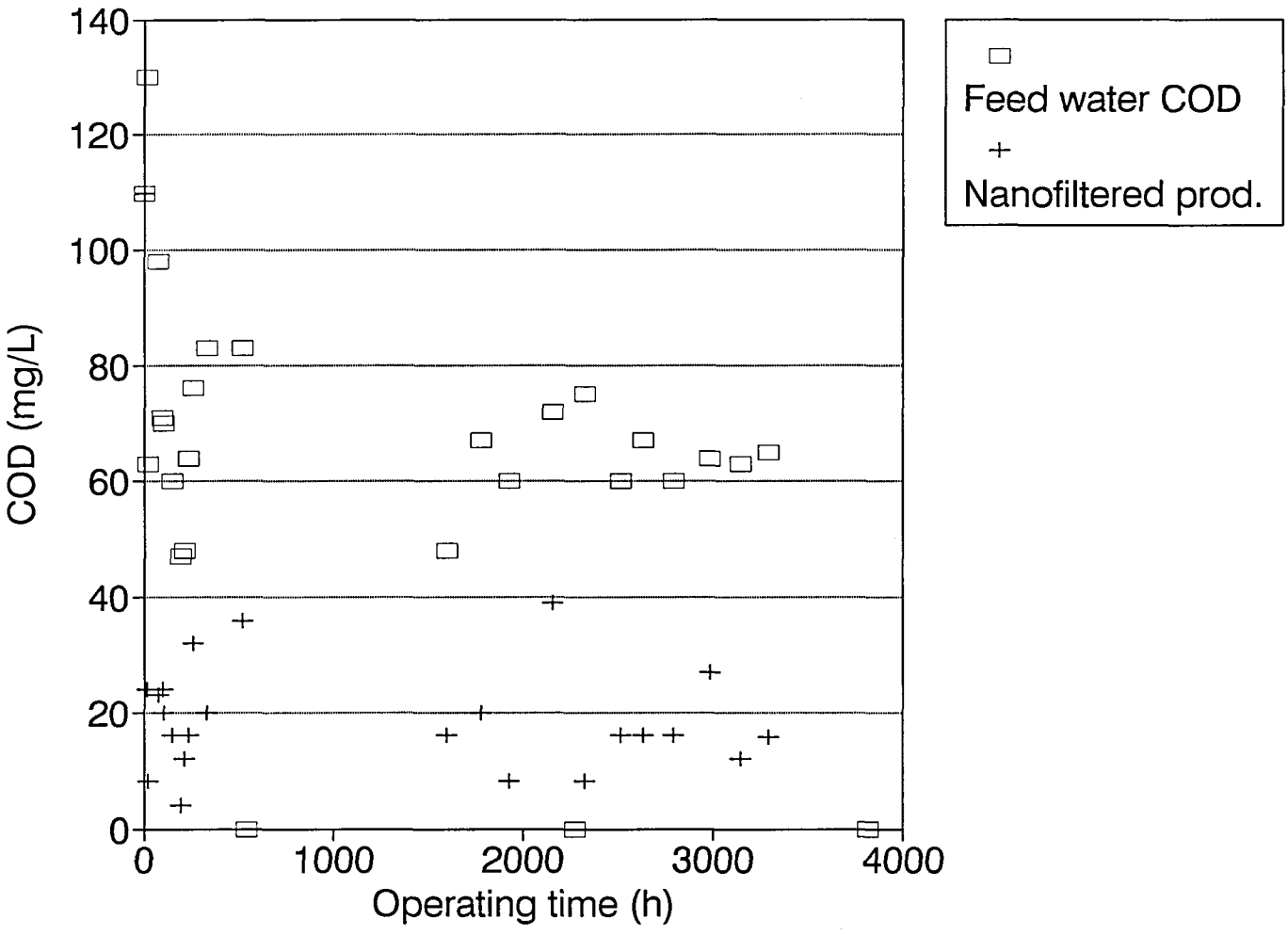

Figure 19: COD load in maturation pond effluent and nanofiltered product

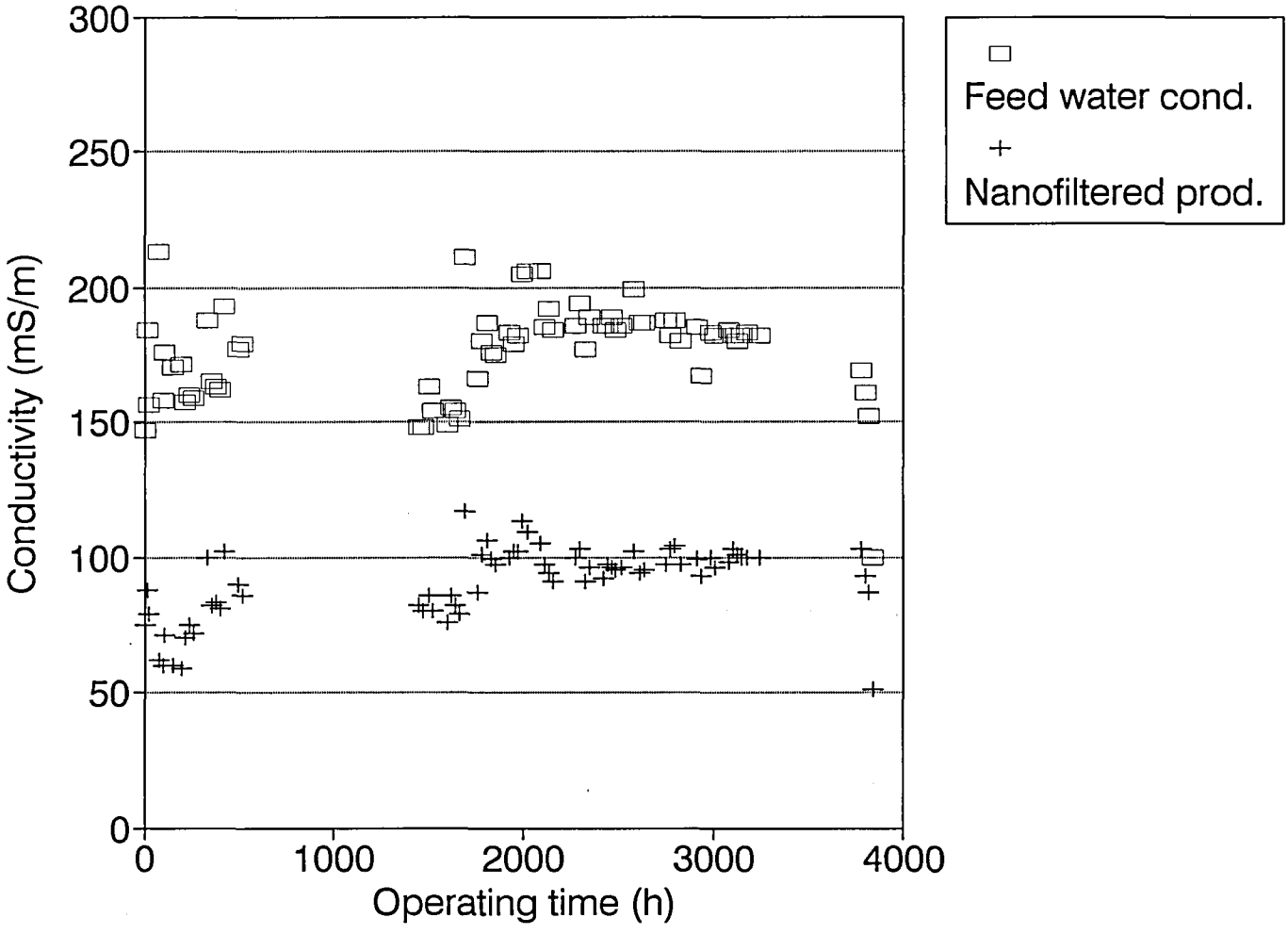

Figure 20: Conductivity of maturation pond effluent and nanofiltered product

cellulose acetate; no acid was added to the incoming water to reduce the pH level to more acceptable values for cellulose acetate membranes.

Salt retention of a fouled membrane was low, but after cleaning the salt retention improved as the flux improved.

The conductivity retention of a fouled membrane was low. However, cleaning restored both the flux and salt retention performance of the membranes.

F. Cleaning regimes

A range of cleaning regimes was used to maintain membrane flux performance. Different detergent flushes and foam ball swabbing were introduced from time to time; a list of the regimes used is shown in Table 7. Organic fouling seemed to be the likely cause of flux deterioration. The LSD64, a product of Lever Bros. showed promise as an alternative detergent for the removal of organic foulants (See Part VI of this report).

Air scouring was also introduced from time to time to loosen colloidal material deposited on the surface of the membranes. The system was pressurized by means of a positive displacement pump and this allowed air to be introduced into the system by venting the suction side of the feed pump.

Table 7: Detergent and other cleaning regimes for nanofiltration membranes

Cleaning regime	Duration
Water flush + 100mg/L NaMetabisulfite	10min
Glint (15%) 5mg/L; pH 7.5	30min
Punch 2%; pH 11	60min
Air scouring	5min intervals; 20min
Punch 2%; pH 11	120min
Biotex 1%	60min
LSD64 1%	120min
SCL 1% flush; Lever *LSD64* 1%	120min

2. ULTRAFILTRATION

A. System design

The capillary membrane test rig was of very simple design and consisted essentially of a feed tank and centrifugal feed and recirculation pumps (Figure 21). A 150μm vortex strainer was installed on the suction side of the feed pump to protect the pump and membranes from blockage by suspended material. The system operating-pressure was controlled by means of a pressure control valve and pressure gauges were used to measure the inlet and outlet pressures. Four 40mm cartridge modules (0,2m^2 membrane area each) were operated during phase I of the programme. The filtration capacity of the plant was increased during phase II of the programme when a 50mm flange-type module (1,0m^2 membrane area) was coupled to the outlet manifold of the four cartridge modules.

The membranes had instantaneous burst pressures exceeding 2MPa, and the system was initially operated at an inlet pressure of 200kPa. The modules were operated at an inlet-to-outlet pressure differential of 50kPa. When the 50mm module was installed, the inlet pressure to the bank of 40mm modules was 250kPa, so as to operate the 50mm module at an inlet pressure of 200kPa. The feed flow volume was maintained at 3 500L/h.

The membranes were operated under constant feed pressure, as opposed to constant flux.

B. Membrane flux

The process flux of the 40mm modules showed a severe and permanent deviation from the pure water flux measured in the laboratory after manufacture (Figure 22 and 23). During the initial stages of the programme the flux was routinely recovered by introducing rigid cleaning protocols. However, after 6 000h of operation, the cleaning procedures followed had a less pronounced effect on flux restoration and the flux eventually stabilized at 20Lmh. Figure 24 shows the typical saw-tooth response that the effective cleaning protocol had on membrane flux during the first 3 000h of operation.

No correlation was found between the flux of the cellulose acetate nanofiltration and polyethersuphone ultrafiltration membranes over the duration of the experiment. This could, in part, be due to the material of membrane construction, cellulose acetate being the more hydrophilic material of the two.

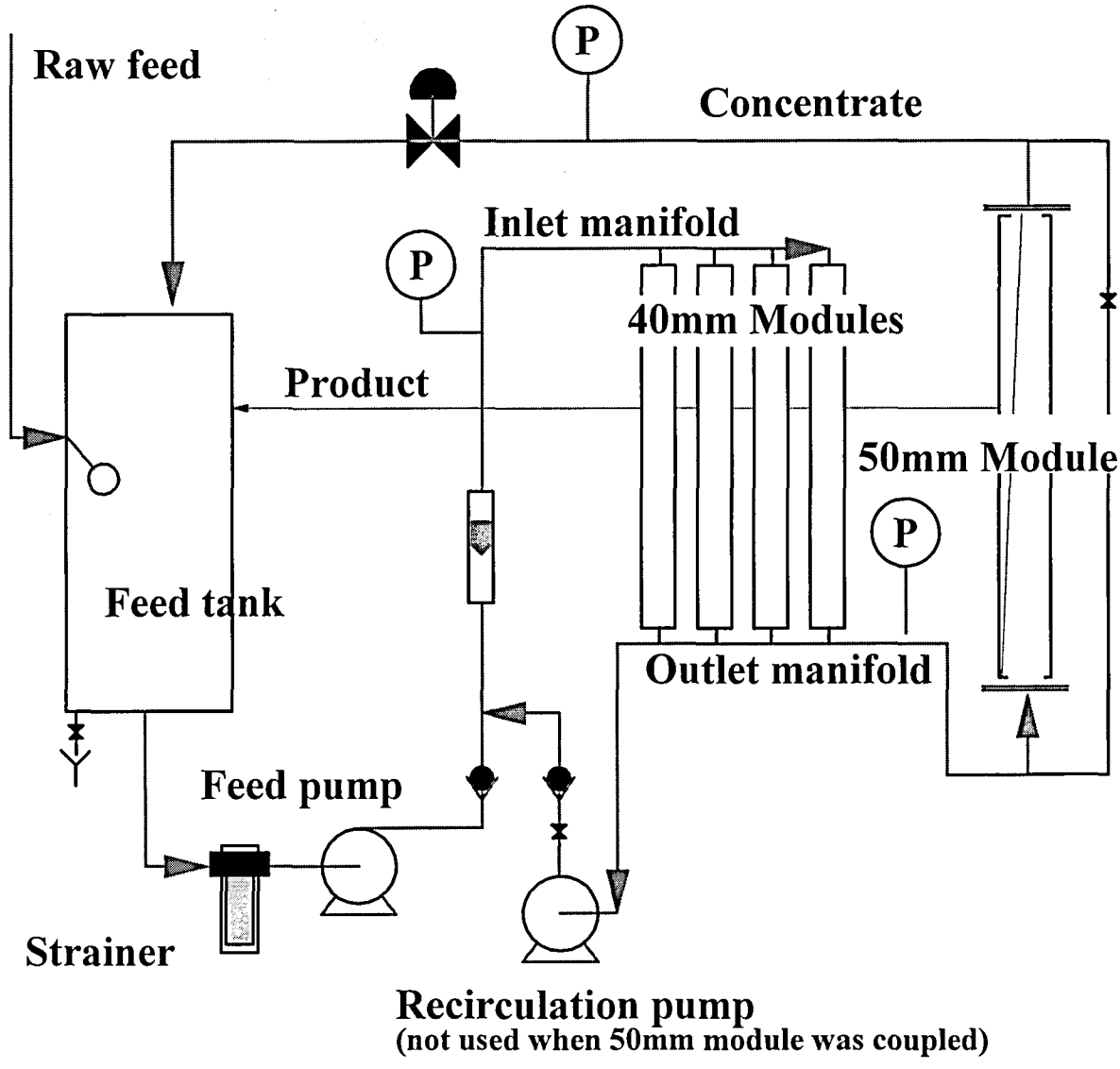

Figure 21: Schematic diagram of the capillary membrane test rig

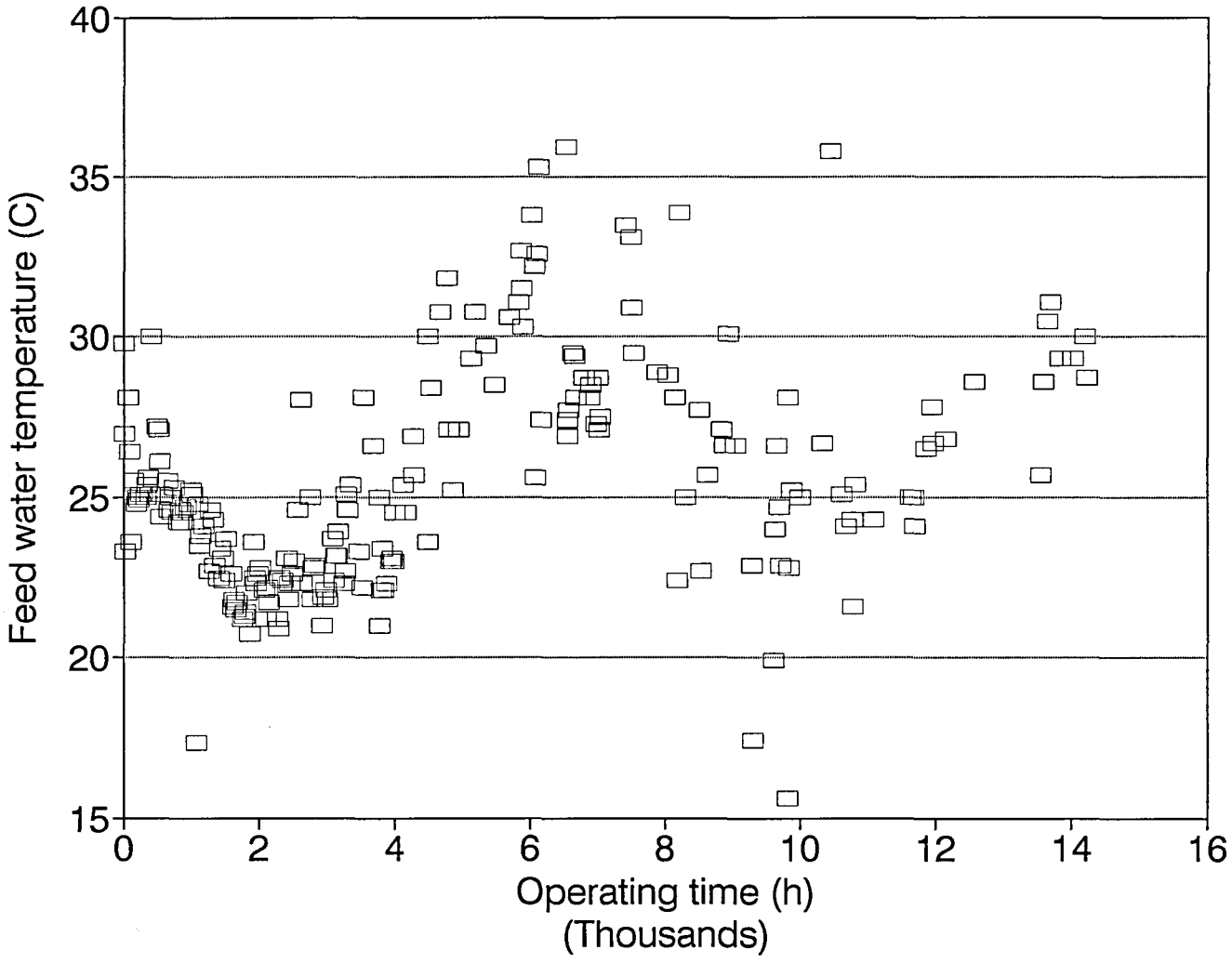

Figure 22: Temperature of the maturation pond effluent feed to the capillary membrane test rig

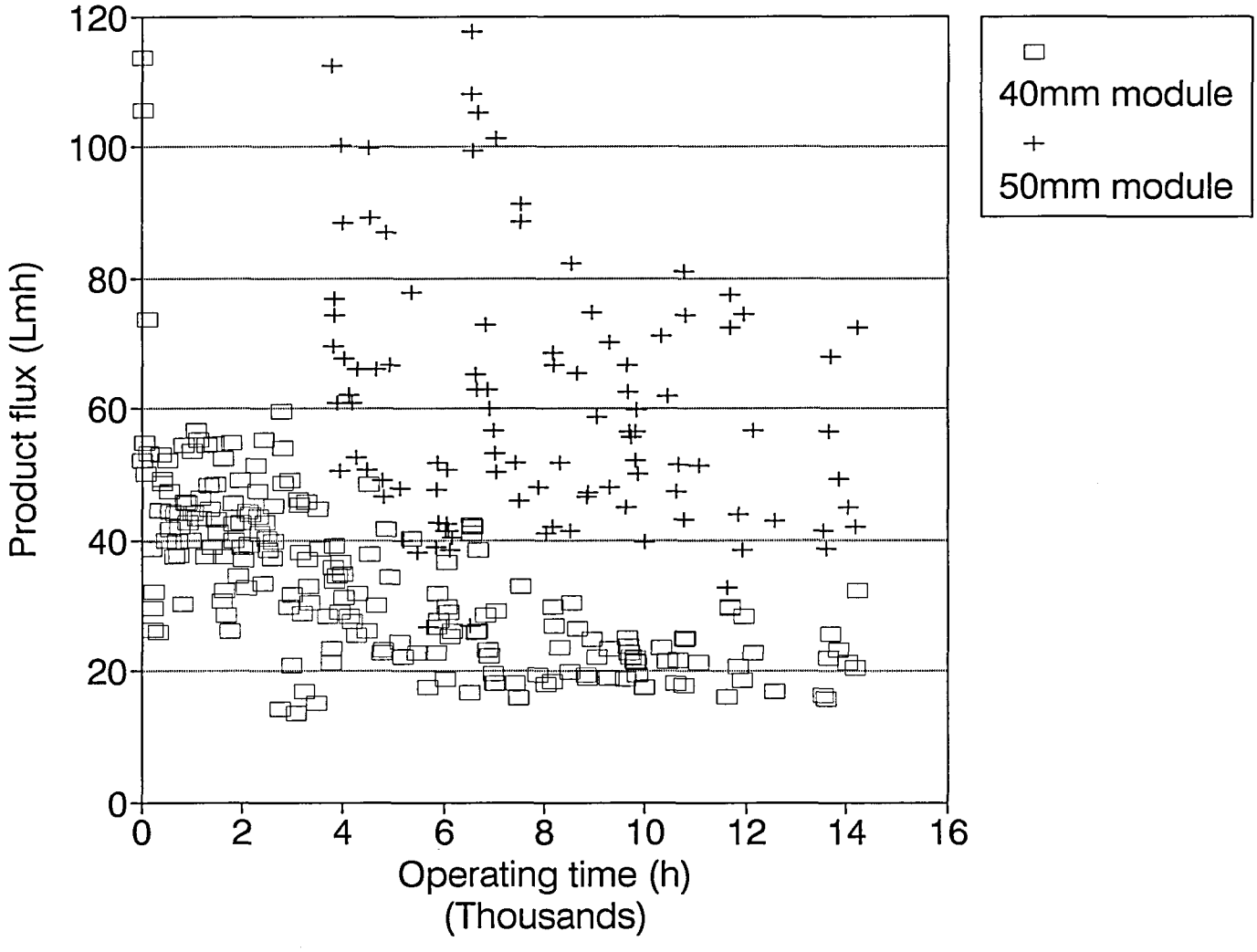

Figure 23: Product flux of the 40mm and 50mm capillary membranes

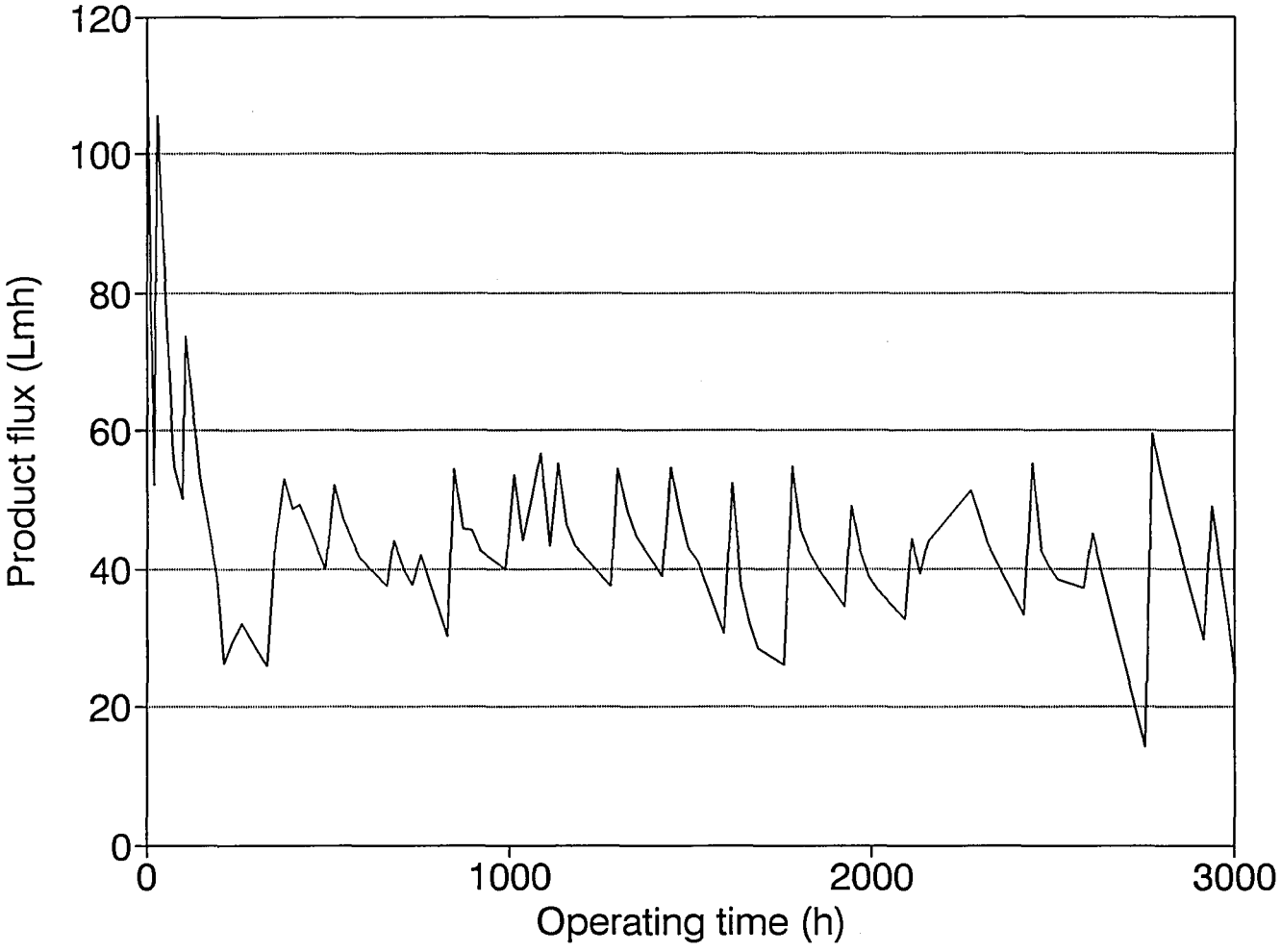

Figure 24: Product flux of 40mm capillary membrane modules over first 3000h of operation

However, module fabrication, membrane morphological considerations and process operation also play roles in membrane flux limitations. Figure 23 shows clearly that the 50mm module outperformed the 40mm modules. Although the membranes both modules were prepared from polyethersulphone, the formulation used to produce the 50mm module membrane was designed to impart slight hydrophilic properties to the membranes. Another important factor in the construction of the two different modules was that the 40mm modules had a transparent shroud, and because the modules were exposed to sunlight for at least part of the day, algal growth had established itself on the outsides of the membranes. A stainless steel shroud was used to encase the membranes in the 50mm module and no algal growth formed on these membranes.

Due to the design of the membrane test plant, no attempts could be made to investigate the effect of intermittant forced backflush on product flux. The system was, however, operated in an on/off mode (60min on, 1min off); 1m static head on the product line. The static back-pressure of 1m was, however, not sufficient to improve the flux performance of the system.

C. Colour removal

The colour of the feed to the ultrafiltration plant is shown in Figure 25 and that of the combined product of the 40mm modules and 50mm module in Figure 26. From these figures it is apparent that the ultrafiltration membranes were capable of reducing the colour content of the water considerably, although nowhere near to the same extent as was achieved with the nanofiltration membranes. The membranes routinely achieved colour retention values exceeding 75%. On average, however, the final product water was still highly coloured and if measured against this variable only, will not be acceptable as a first-grade water. The high colour content of the feed water was probably caused by the presence of textile dye effluent.

D. COD reduction

The ultrafiltration membranes reduced the COD content of the feed water (see Figure 27), but with colour reduction, the performance of these membranes were not as good as that of nanofiltration. A large fraction of the organic species present in the maturation pond effluent was of low molecular mass, and a large reduction in their concentration would not be expected. However, the membranes did reduce COD by about 50%, which could indicate the presence of a secondary membrane-layer on the surface of the capillary membranes (formed

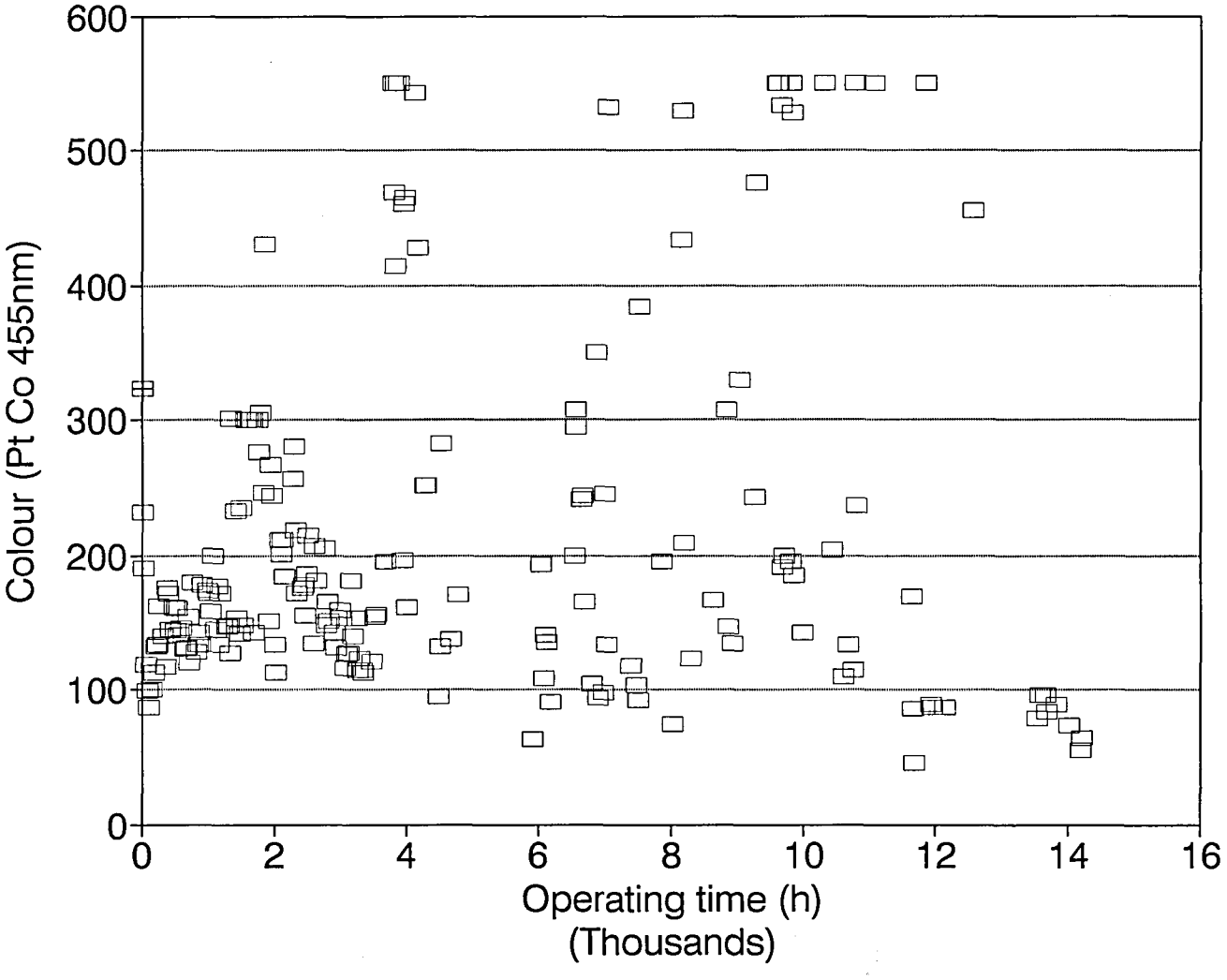

Figure 25: Colour content of the maturation pond feed to the ultrafiltration plant

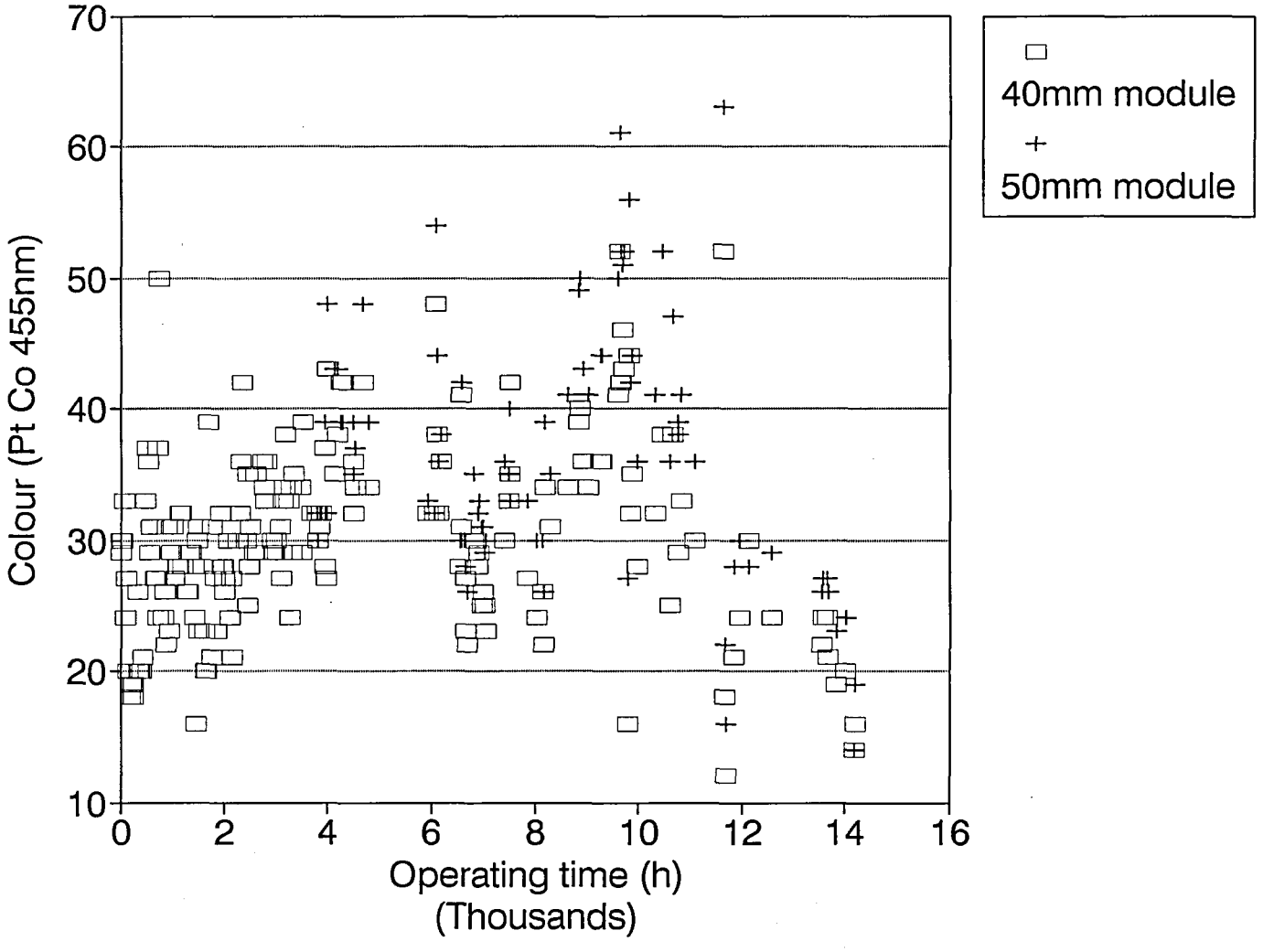

Figure 26: Colour content of the ultrafiltered product

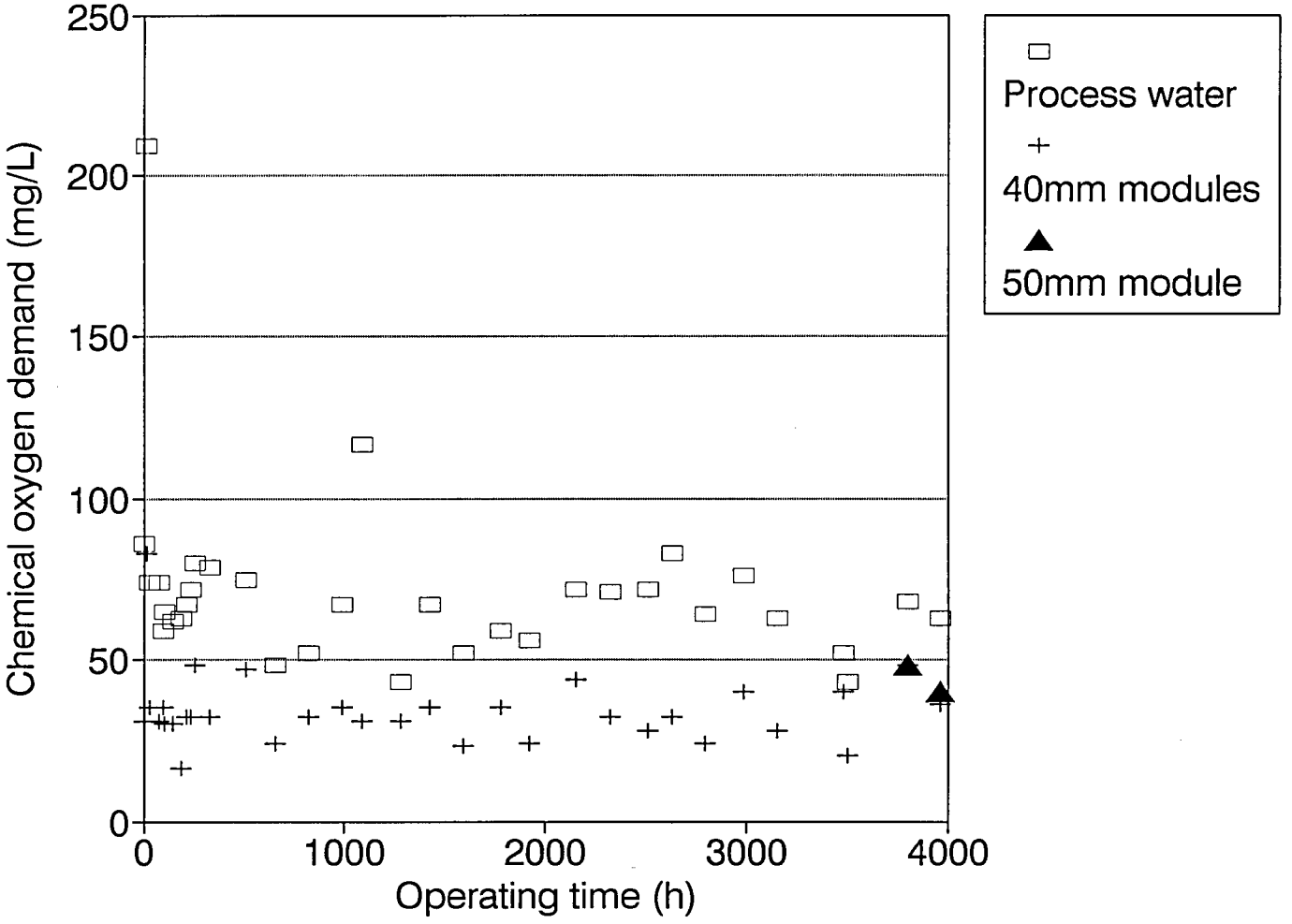

Figure 27: Chemical oxygen demand of the maturation pond feed water and ultrafiltered product

as result of concentration polarization), as well as the presence of larger-sized recalcitrant molecules in the feed water which were not altered in size by the biological treatment operation.

COD measurements were discontinued after 4 000h because of restricted laboratory time allocation for these determinations.

E. Turbidity removal

The ultrafiltration membranes produced a final clear product of very low turbidity as can be seen in Figure 28 which also illustrates that the turbidity of the filtered product is not coupled to the turbidity of the feed water, and that turbidity values of less than 0,2NTU could be achieved consistently. This correlated to turbidity reduction rates greater than 95%.

F. Microbial indicators

The nanofiltration and ultrafiltration membranes did not prove to be a sterile filtration barrier as indicator organisms were found to be present in the filtered product of both processes. This could be due to product line recontamination, that is, reverse infiltration of the organisms through the product output line. It could also be the result of poor membrane manufacture which would result in pin-holes or large-sized pores in the skin-layers of the membranes. However, both membrane filtration processes reduced microbial counts.

If one were to accept this as fact, the question was to what extent did the product water need to be chlorinated to ensure a disinfected product? In one experiment, different concentration levels of chlorine was introduced to 200ml samples of the nanofiltered and ultrafiltered products, and stirred in a closed container for a period of 60min. The residual chlorine was destroyed after this contact period and the samples were tested for the presence of total and feacal coliform plate counts. The data for two experiments are shown in Table 8. From this data it shows that different chlorine demands was necessary to achieve disinfection. The demand decreased in the order feed>ultrafiltered product>nanofiltered product.

G. Cleaning regimes

The poly(ether sulphone) ultrafiltration membranes are hydrolytically more stable than cellulose acetate membranes, and for this reason more stringent cleaning protocolscould be

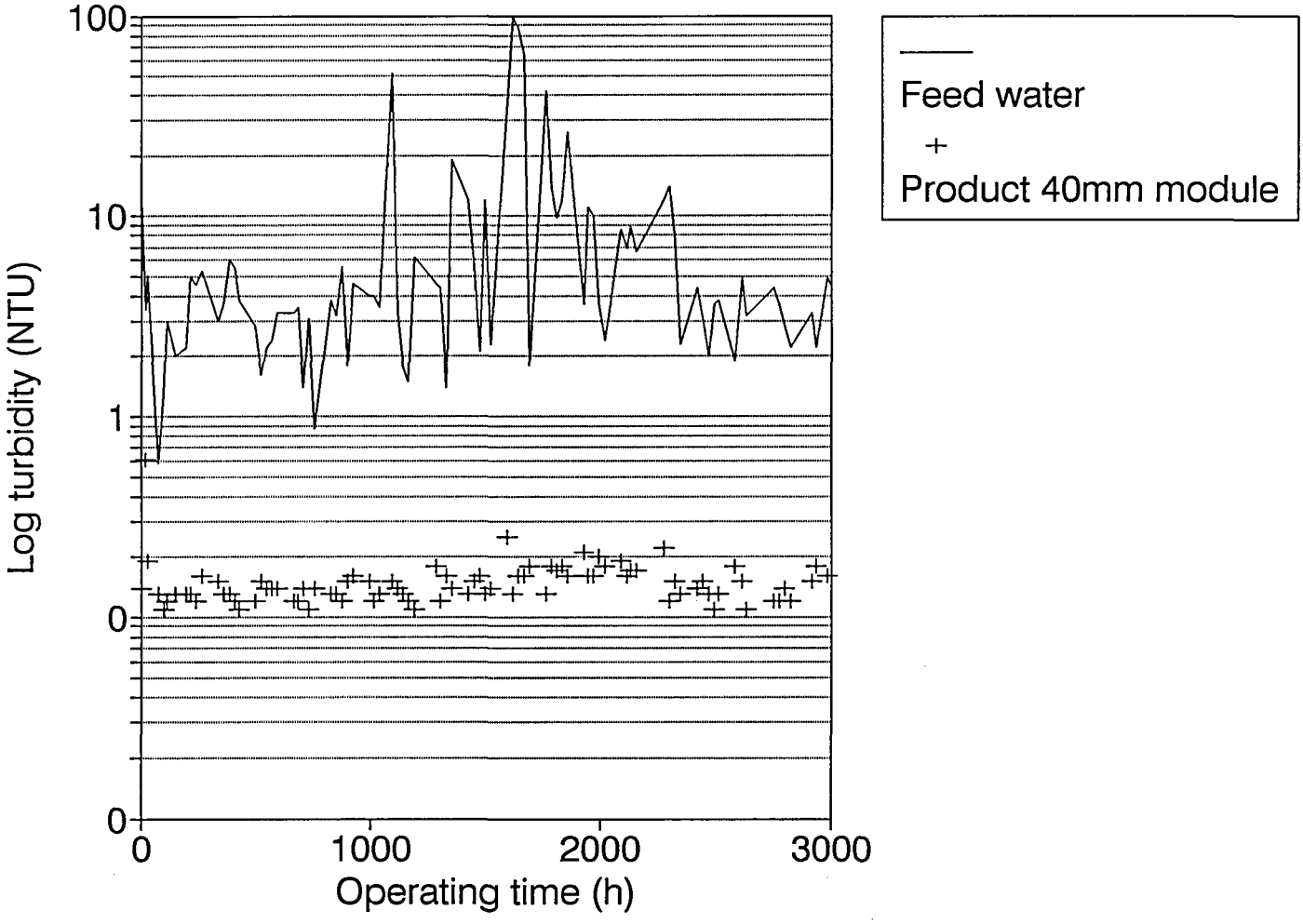

Figure 28: Turbidity removal efficiency of the ultrafiltration process

devised. Table 9 gives a list of the different cleaning procedures used. Unfortunately, although capillary membranes can be backflushed (i.e. by reversing the direction of product flow through the membrane wall), the plant design did not include this option. On occasion, however, individual modules were removed and backflushed manually with tap water for 5min.

Table 8: Chlorine demand of nanofiltered and ultrafiltered product

Sample	Type	Chlorine	Experiment 1		Experiment 2	
		mg/L	Feacal coli	Total coli	Feacal coli	Total coli
1	A	0	14	400+	0	TNC
2	A	2	2	65	0	TNC
3	A	4	2	27	0	24
4	A	6	0	37	0	14
5	A	8	0	37	0	8
6	A	10	0	31	0	1
7	B	0	55	213	0	18
8	B	0.5	1	68	0	17
9	B	1	0	1	0	1
10	B	1.5	0	2	0	0
11	B	2	0	2	0	1
12	B	2.5	0	0	0	0
13	C	0	0	1	0	36
14	C	0.25	0	0	0	3
15	C	0.5	0	2	0	0
16	C	0.75	0	2	0	0
17	C	1	0	1	1	12
18	C	1.25	0	1	0	0

A: Maturation pond effluent, B: 50mm Ultrafiltration module product, C: Nanofiltration product
TNC: too numerous to count

None of the cleaning regimes used had any detrimental effect on the integrity of the membranes, but some permanent flux loss was observed over the full duration of the experiment. This could have been caused by permanent pore blocking or irreversible fouling of the membrane surface. No autopsy was performed on the membranes to determine the reason for low product yields towards the end of the experiment, or of the the poor recovery of product flux after cleaning.

Table 9: Cleaning regimes for ultrafiltration membranes

Protocol	Duration
Clean water rinse	20min
SCL 1g/l	10min
NaOH pH 12 + SCL 1g/l	10min ea
Punch 2%, pH 11	30min
Punch 2%, pH 11	60min
Punch 2%, pH 11	120min
Punch 2% + SCL 1g/l	20min ea
Biotex 2%	60min
Biotex 2% + *Punch* 2%	60min, 120min
Sanochlor 7,5ml/l + EDTA 2g/l	30min, 120min
Biotex 2%	600min
Sanochlor 10g/l	20min
Biotex 2% + *Sanochlor* 10g/l	120min, 30min
Sodium lauryl sulphate 0,5% + *Sanochlor* 1%	90min, 30min
Acid wash pH2 + *Lever Ind LSD64* 1% pH 9.7	10min, 960min
LSD64 1% + acid rinse pH2	120min, 10min
Acid wash pH2 + *LSD64* 1%	10min, 120min
Acid rinse pH2 + *LSD64* 2% pH 9.7	10min, 960min
LSD64 2% pH 9.7	120min
LSD64 2% pH 9.7 + *Sanochlor* 100mg/l + acid rinse	120min, 20min, 10min

V. EVALUATION OF AN ALTERNATIVE DETERGENT AS CLEANING AGENT

A Lever Bros detergent (*LSD64*) was tested as a cleaning agent during the evaluation of the nanofiltration membranes on maturation pond effluent. The flux of the nanofiltration membranes was restored with the new detergent. However, it was deemed necessary to evaluate the detergent on reverse osmosis membranes as well, since it was argued that if the detergent had any adverse effect on membrane performance, reverse osmosis membranes would be more sensitive and would sooner indicate any transient effects on performance.

A study was therefore conducted to compare the effect of prolonged contact with *Biotex* and *LSD64* on the salt-retention and flux performance of cellulose acetate tubular reverse osmosis membranes. The object was to determine whether *LSD64* could be used as a viable alternative or to replace *Biotex* which is the generally recommended and used detergent.

1. EXPERIMENTAL

A. Samples

TRO CA membranes were obtained from Envig (Pty) Ltd. The membranes were taken ar random from the production line after they had been annealed. The membranes were removed before the quality control station at Envig (Pty) Ltd.

B. Test procedure

Six 1m-long membrane sections, connected in series, were tested in the following way:

- ❑ Precompaction test: 4h at 4MPa, tested against 2g/L NaCl at a linear velocity of 1m/s and a temperature of 20°C. The salt-retention performance (conductivity retention) and water flux were determined. These results were used as the base-line performance.
- ❑ The membranes were next subjected to a pure water flux (PWF) test, in which the membranes were tested against pure water at a feed pressure of 2MPa and linear velocity of 1m/s.
- ❑ The feed tank was charged with 0,5% by mass of the selected detergent, without pH adjustment or the addition of any further chemicals. The system was operated at a feed pressure of 2MPa and a linear velocity of 1m/s during the detergent contact cycle of operation.
- ❑ The detergent contact test was continued for a day when the feed solution was rinsed from the system and replaced with pure-water. The membranes were again tested against the 2g/L NaCl feed solution and the cycle of tests repeated.
- ❑ The tests were terminated after >100h accumulated exposure time.
- ❑ Biotex (pH 8.6) and LSD64 (pH 10.3), the latter a product of Lever Industries, Boksburg, were used in the tests.
- ❑ The tests were conducted at both 20°C and 30°C.

C. Results

The pure water flux (PWF) performance and the NaCl retention and RO flux performances are shown in Table 10 for the *Biotex* (20°C and 30°C) and *LSD64* (20°C and 30°C) tests.

D. Discussion

Close inspection of the results indicates that the detergents had no significant effect on the performance of the membranes. There is no clear indication that any of the detergents affected membrane performance adversely.

Table 10: Performance of membranes in contact with *Biotex* and *LSD64*

Accum. [h]	RO flux @ 2g/L, 4MPa,1m/s [Lmd]						RO conducivity retention @ 2g/L, 4MPa, 1m/s [%]						Pure-water flux, 2MPa, 0,5m/s [Lmh]					
	1	2	3	4	Mean	Std. Dev	1	2	3	4	Mean	Std. Dev	1	2	3	4	Mean	Std. Dev
LSD64 20°C																		
0	24.6	30.3	28.3	26.5	27.4	2.1	97.7	96.5	97.6	97.3	97.3	0.5	16.1	20.8	18.8	17.4	18.3	1.7
23.6	23.7	29.3	27	25.4	26.4	2.1	97.9	97.1	98.1	97.8	97.7	0.4	15	18.8	16.9	16.2	16.7	1.4
45.8	24	29.8	27.3	26.2	26.8	2.1	97	96	97.6	97.1	96.9	0.6	14.7	18.6	16.8	16.2	16.6	1.4
71.1	23.4	28.8	26.5	25.4	26.1	2.1	97.3	97	98	97.5	97.4	0.4	14.7	18.2	16.8	16.1	16.5	1.3
117.2	23.7	29.4	28.3	25.8	26.8	2.2	97.2	96.6	97.9	97.5	97.3	0.5	14.7	18.2	16.8	16	16.4	1.3
141.5	24.2	30.1	27.7	26.3	27.1	2.1	97.9	96.5	97.8	97.4	97.4	0.5	14.6	18.2	16.9	15.7	16.3	1.3
159.7													14.5	18.1	16.6	15.8	16.3	1.3
LSD64 30°C																		
0	30.7	26.2	28.4	31.4	29.2	2.1	98.3	98.4	98.4	98.1	98.3	0.1	20.4	16.3	17.4	21.7	19	2.2
23	32.4	25.4	28	31.9	29.4	2.9	98.3	98.4	98	98.1	98.2	0.1	20.5	16.4	17.7	21.8	19.1	2.1
46.1	32.1	25.1	27.2	34	29.6	3.6	98	98.6	98.2	97.9	98.2	0.3	20.7	16.1	17.7	22	19.1	2.3
69.4	32	25.1	27.3	34.2	29.6	3.6	98	98.6	98	97.8	98.1	0.3	20.7	15.9	17.6	22.1	19.1	2.4
92.7	32.7	25.3	27.5	34.7	30.1	3.8	97.9	98.6	98	97.8	98.1	0.3	20.9	16.2	17.7	22.3	19.3	2.4
112.3													21.5	16.4	18	22.8	19.7	2.6
Biotex 20°C																		
0	24	25.1	24.8	22.1	24	1.2	95	97.2	97.8	97.3	96.8	1.1	18.9	19.3	19.2	16.6	18.5	1.1
22.8	24.6	25.8	25.1	22.7	24.6	1.2	97.9	97.1	98.1	97.8	97.7	0.4	17.2	16.9	16.4	14.7	16.3	1
45.1	23.5	24.5	23.9	21.6	23.4	1.1	96	97.7	97.2	98.3	97.3	0.8	16.2	16.8	16.3	14.6	16	0.8
68.8	24	25	24.4	22.2	23.9	1	95.7	97.8	97.2	98.3	97.2	1	16.2	16.6	16.2	14.4	15.9	0.9
116.5	23.6	24.7	23.9	21.7	23.5	1.1	95.9	97.7	97.1	97.5	97.1	0.7	15.7	16.4	16	14.2	15.6	0.8
139.6	23.8	24.8	24.4	22	23.7	1.1	95.3	97.6	96.9	98.2	97	1.1	15.8	16.2	15.8	14.2	15.5	0.8
159.2													15.6	16.1	15.8	14.2	15.4	0.7
Biotex 30°C																		
0	27.2	31.9	33.1	29.4	30.4	2.3	98.7	98.4	98.4	98.5	98.5	0.1	17.1	20.5	21.2	18.9	19.4	1.6
25.4	26.3	31.2	32.9	29	29.8	2.4	95.7	98.3	98.2	98.4	97.6	1.2	17.7	21	22	19.6	20.1	1.6
50.2	26.2	30.7	32.5	28.5	29.5	2.4	97.1	98.4	98.3	98.5	98.1	0.6	17.1	20.4	21.5	18.8	19.5	1.7
72.7	26.2	30.7	32.5	27	29.1	2.6	97.1	98.1	98	98.2	97.8	0.4	17	20.1	21.3	18.8	19.3	1.6
96.5	25.4	29.5	31.3	27.9	28.5	2.2	98.4	98.2	97.9	98.1	98.2	0.2	16.2	18.5	19.7	17.7	18	1.3
1148													16.8	19.7	20.8	18.5	18.9	1.5

VI. CONCLUSIONS

- ❑ The ultrafiltration capillary and nanofiltration tubular membranes performed well during the studies and no problems were experienced with their integrity over the 16 000h period tested.
- ❑ The turbidity of the ultrafiltered product was very low. The membranes showed good colour-removal capabilities, but the colour of the filtered product was still higher than the maximum specified for potable water.
- ❑ The COD load in the ultrafiltered product was low, but not as low as that in the nanofiltered product.
- ❑ The flux performances of the 40mm and 50mm modules did not correspond. The membranes were produced from the same formulation, but the fabrication protocol was slightly different. It should therefore be possible to improve the flux performance of the capillary membranes, without decreasing the retention performance, by modifying the membrane formulation and fabrication protocol.
- ❑ The 40mm capillary membrane cartridge modules performed well. No leaks occurred between the tubesheet and the module shroud as the seal remained intact. The design of the 50mm stainless steel capillary membrane cartridge module also proved to be adequate to sustain long-term use.
- ❑ The stainless steel shroud of the 50mm module proved to be an advantage as no algal growth appeared on these membranes, as happened to the 40mm modules which had transparent shrouds.
- ❑ u-PVC proved to be an adequate and inexpensive material for use in the construction of module shrouds. However, the u-PVC material did impose an upper operating temperature limit of 40°C.
- ❑ The performance of the nanofiltration membranes declined with time. This was ascribed to hydrolysis of the cellulose acetate membranes as no acid was used to adjust the pH of the feed water to a more suitable level.
- ❑ The quality of the nanofiltered water was very high, and nanofiltration could be useful for the treatment of secondary treated sewage, to produce high quality water for industrial use.

VII. RECOMMENDATIONS

The capillary ultrafiltration membranes performed well during the experiments and their relevance in potable water production and effluent treatment should be investigated further. There are, however, aspects of the present technology that should receive attention. These are summarized below:

- ❑ Membrane fouling could be a deterent in the use of membrane filtration technology. The development of *antifouling* precoats should be investigated as it would not only shorten intervals between membrane cleaning, but would also

reduce the harshness of the protocol required to clean the membranes. This applies equally to nanofiltration and ultrafiltration.

- ❑ Low-cost modules and manifolding should be developed. Special attention should be given to increasing the membrane area in these modules. The modules and manifolding system should be designed so as to simplify module removal for ease of membrane replacement and other reasons.
- ❑ The use of ultrafiltration to upgrade industrial effluents should be investigated on a larger scale (20 to 40m^2 membrane area).
- ❑ The use of ultrafiltration to upgrade surface water to standards set for drinking water should be investigated on a larger scale. The possibility of using a standard approach to the treatment of waters with different turbidities should be investigated. It is very important that indicator micro-organisms should be monitored very regularly during such experiments so as to determine the efficiency of the membranes as absolute filtration barriers.
- ❑ Attention should be given to the development of a standardized microbial or virus indicator test to monitor the removal/reduction efficiency of ultrafiltration membranes in potable water production applications or as a quality control measure during membrane manufacture.
- ❑ A cost study should be conducted to determine the specific cost to treat surface water to drinking water standards.

VIII. TECHNOLOGY TRANSFER

The results obtained in this study indicated that the capillary ultrafiltration membranes and module prototypes developed at the Institute of Polymer Science were useful for water clarification and colour reduction. As an extention of the work conducted in this programme, the ultrafiltration membranes were tested in larger-sized modules at Mon Villa (WRC project KV/184: *Research on rural and peri-urban water supply*). The 90mm modules used had a membrane area of 4m^2 and were an upscaled version of the 40mm module design tested at Uitenhage. The inlet and outlet manifolds of the 90mm modules had similar T-piece designs similar to those used at Uitenhage.

The results of the trials at Mon Villa demonstrated the usefulness of ultrafiltration capillary membranes as a one-step treatment option for potable water production. The raw water treated at Mon Villa had an incoming colour content that ranged between 40 and 60 Hazen units. A surprising result was that the membranes were capable of producing a final water with a colour content below 5 Hazen. These results lead to further investigations and in a collaborative WRC programme (WRC project K5/764: *Research into water supply to rural and peri-urban communities using membrane technologies*), which involved co-operation

from the Chemical Engineering Department of ML Sultan Technikon, it was demonstrated, at Suurbraak in the South Cape, that the membrane process was capable of reducing the colour content of the incoming water from Hazen colour units of as high 600 to values of below 10. The water recovery ratios achieved at Suurbraak often exceeded 85%, and in which case the concentrate had colour values exceeding 2000 Hazen units.

A pilot plant operating on six 90mm capillary ultrafiltration membrane modules is currently being tested at the Windhoek Goreangab reclamation plant, to determine the capability of the membranes to remove protozoan cysts and o-ocysts from the reclaimed water. The membranes are producing good quality water, with turbidity values often as low as 0,06 NTU.

Although the ultrafiltration process is still under development and much R&D is essential to improve the membranes, modules and process, Umgeni Water has expressed an interest in commercializing the technology. A pilot plant which can acommodate up to twelve 90mm modules has been constructed by Umgeni Water, in collaboration with the Chemical Engineering Department of ML Sultan Technikon, to test the process on various feed waters.

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