FINAL REPORT

RESEARCH AND DEVELOPMENT OF POLYMERS FOR THE FORMATION OF DYNAMIC MEMBRANES AND THE EVALUATION THEREOF OR THE TREATMENT OF INDUSTRIAL EFFLUENTS

by

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FINAL REPORT

RESEARCH AND DEVELOPMENT OF POLYMERS FOR THE FORMATION OF DYNAMIC MEMBRANES AND THE EVALUATION THEREOF FOR THE TREATMENT OF INDUSTRIAL EFFLUENTS

PART I

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SECTION A : INVESTIGATIONS ON 0,02 m^2 POROUS STAINLESS STEEL TUBES AND NON-WOVEN FABRIC TUBES

1 DYNAMICALLY FORMED HYDROUS ZIRCONIUM (IV) OXIDE/POLYACRYLIC MEMBRANES; LOW PRESSURE FORMATION, HIGH PRESSURE EVALUATION

1.1 Naked Porous Stainless Steel Tubes (CARRE Inc.)

Investigations were carried out on the formation of composite membranes prepared at low pressure on naked porous stainless steel tubes (CARRE Inc.). The tubes had the following dimensions:-

internal diameter, 14 to 15 mm; external diameter, 21,3 mm; effective porous length, 45,5 mm; effective internal surface area, 0,02 m^2.

Such membranes when tested against solutions of 2 000 mg/ℓ sodium nitrate at pH near 7 and at 6 000 kPa inlet pressure yielded flux values of 150 to 300 ℓ/m^{2}h and rejection values (Robs) of 60 to 70 % at high cross-flow velocities.

1.2 Pretreated Stainless Steel Tubes (CARRE Inc.) Using Fumed Silica

When the pore size of the tubes was modified by "pore filling" with a fumed silica suspension (Cab-O-Sil), the degree of reproducibility of results in tests at 600 kPa improved markedly. The composite membranes prepared and tested at 600 kPa and 1,25 m/s cross-flow velocity on such pretreated tubes gave consistent flux values near to 60 ℓ/m^{2}h and rejection values near 30% for solutions containing 2 000 mg/ℓ $NaNO_3$ at pH near 7.

When operated at higher pressures (6 000 kPa), the high permeate flux results in polarisation and cross-flow velocities need to be increased. At 6 000 kPa and a cross-flow velocity of 4,3 m/s, flux values over 500 ℓ/m^{2}h and rejection values of about 60% can be achieved.

At formation pressures of 2 000 kPa, the indications were that slightly better membranes formed with flux values approaching 600 ℓ/m^{2}h and rejection values above 60 % and this aspect is followed up later in the report.

When, however, the fumed silica was added to the hydrous zirconium (iv) oxide suspension during zirconium membrane formation, the hydrous zirconium (iv) oxide membrane (zirconium membrane) and the subsequently formed zirconium/ polyelectrolyte membrane behaved as membranes on naked tubes.

It was thus demonstrated that prior pore filling of porous stainless steel tubes (CARRE Inc.) with colloidally dispersed silica improved the reproducibility of results and assisted in producing a high flux membrane which could be formed at low pressure (600 - 2 000 kPa) and subsequently used at high pressure.

The above investigations are fully described in a paper (1) presented at the International Membrane Technology Conference, 15-17 November 1988, in Sydney, Australia and in a contribution (2) to the Workshop on Desalination and Membrane Processes, Ohrigstad, 24-26 August 1988 (Appendix 1).

1.3 Pretreated Porous Stainless Steel Tubes Using Zirconium Oxides

In view of the excellent results achieved on stainless steel tubes precoated with a dilute suspension (2 mg/ℓ) of fumed silica, it was decided to determine the effect of two other suspensions, also at a concentration of 2 mg/ℓ:-

a) zirconium oxide prepared from basic zirconium carbonate.

b) hydrous zirconium oxide precipitate prepared from a zirconium nitrate solution at pH >6 and then well dispersed in water.

Zirconium oxide (a) did not cause any significant decline of the pure water flux. The hydrous zirconium oxide precipitate (b), however, caused a significant flux decline from over 20 000 ℓ/m^{2}h at 600 kPa to a steady flux after one hour, of about 2 700 ℓ/m^{2}h (2 mg/ℓ suspension in 50 ℓ water).

The flow through the tubes was even over the length. The behaviour of the hydrous zirconium oxide precipitate was very similar to that observed with a suspension of silica. This is not unexpected if the nature of the hydrous zirconium oxide suspension is compared with that of the fumed silica suspension (Cab-O-Sil).

A typical Cab-O-Sil surface contains co-valently bonded hydroxyl and siloxane groups. When this material is dispersed in liquids, the surface hydroxyl can link the individual aggregates together through bonding into intricate three dimensional networks. These relatively weak hydrogen bonds are disrupted by shearing action but re-establish themselves on standing at rest.

When sodium hydroxide is added to a zirconium nitrate solution, in sufficient excess, an amorphous precipitate, commonly called hydrous zirconia, forms. It is considered that zirconium atoms are bonded by "ol" bridges which may under certain conditions convert to oxobridges. This base precipitation occurs so rapidly that random polymer structures are formed as distinct from the orderly structure formed during slow formation of hydrous zirconium oxide.

The hydrous zirconium oxide can be regarded also as consisting of three-dimensional aggregates of indefinite shape and sizes comprising vast numbers of very loosely bound water molecules surrounding reactive hydroxyl groups and some aquagroups which are co-ordinately bound to tetramers of zirconium atoms. The zirconium atoms of the tetramers are linked, both internally and to zirconium atoms of the tetramers, by less reactive bridging pairs of hydroxyl groups or by still less reactive oxygen atoms (3,4).

Tests on membrane formation were carried out on a stainless steel tube pretreated with a suspension of a hydrous zirconium oxide precipitate (hydrous zirconia) (2 mg/ℓ). A zirconium membrane was laid down in the usual manner followed by chelation with polyacrylic acid. These membranes were prepared at 600 kPa but evaluated at high pressures. Results are given in Table 1.

TABLE 1

Membranes Prepared on Tube Pretreated with Precipitated Hydrous Zirconium Oxide

Test	Date	Membrane	Tube	Inlet pressure kPa	Flux ℓ/m^{2}h	Rejection* %	Cross-flow velocity m/s
2013	23/09/88	-	T4	600	- precoating -		1,25
2014	29/10/88	Zr	T4	600	213	18,5	1,25
2015	02/10/88	Zr/PAA	T4	600	55	35	1,25
2016	04/10/88	Zr/PAA	T4	850	37	-	1,70
				2 000	140	56	3,70
				3 000	207	62	4,10
				6 000	366	65	3,80

* Rejection from solution containing 2 000 mg/ℓ $NaNO_3$;
for Zr membrane pH 3,5
for Zr/PAA membrane pH 6,8 - 7,2.

These results compare favourably with results obtained when fumed silica was used as the pretreatment material. It is considered that pretreatment with hydrous zirconia will be more satisfactory in practice since the tubes can be stripped readily with nitric acid alone. Tubes pretreated with fumed silica are best cleaned with sodium hydroxide and hydrogen peroxide solution, followed by nitric acid solution.

1.4 Comparison of Membranes on Pretreated and on Naked Tubes

A series of tests with membranes prepared on naked and on pretreated tubes was conducted to confirm trends already shown. The pretreated tubes were treated either with a suspension (2 mg/ℓ) of fumed silica or a suspension (2 mg/ℓ) of hydrous zirconia. The tests were carried out at formation pressure of 600 kPa and at 2 000 kPa. Evaluation was carried out at 2 000 kPa, 3 000 kPa and 6 000 kPa. The detailed results are given in Appendix 2 (Tests A to K). A summary of the results is given in Table 2.

It is interesting to note that the silica pretreatment resulted in membranes with good stability. These membranes reached final flux and reject values rapidly after change in pressure conditions. This was not the case with membranes on naked tubes. The membranes on tubes pretreated with hydrous zirconia responded reasonably well, also achieving final flux and reject values fairly rapidly.

TABLE 2
Summary: Composite Membranes Zr/PAA on Porous Stainless Steel Tubes

Series	Test	Pretreatment pressure kPa	Inlet formation pressure kPa	Test pressure kPa	Cross-flow velocity m/s	Flux ℓ/m^2h	Rejection %	Conductivity of feed mS/cm
Naked Tubes								
E	1025/31	-	600	6 000	3,8	180	67	-
F	1087/89	-	2 000	6 000	3,9	110	55*	2,25
G	2023/24	-	6 000	6 000	3,7	87	66	2,20
Tubes pretreated with silica								
	1075	600	600	6 000	4,3	522	56	-
A	1074/76	600	600	6 000	4,3	504	59	2,40
B	1085/88	2 000	2 000	6 000	4,2	585	67	2,25
H	2025/27	1 000 - 6 000	6 000	6 000	3,9	230	72	2,34
I	2029/25	4 000	6 000	6 000	4,3	250	80	2,25
I	2030/36	4 000	6 000	6 000	4,3	240	81	2,28
Tubes pretreated with hydrous zirconia								
C	2013/16	600	600	6 000	3,7	366	65	2,34
D	2017/22	2 000	2 000	6 000	3,9	294	67	2,27
D	2019/21	2 000	2 000	6 000	3,9	333	68	2,25
J	2039/40	4 000	6 000	6 000	4,3	165	82	2,43
J	2041/43	4 000	6 000	6 000	4,3	195	80	2,30
K	2044/46	4 000	4 000	6 000	4,1	264	80	2,23
K	2050/52	4 000	4 000	6 000	4,3	165	88	2,34

* Unstable in changing from lower to higher pressure.

It would appear that pretreatment at 2 000 - 4 000 kPa and membrane formation at similar pressures will yield membranes of high flux and good rejection. A certain amount of tailoring could be undertaken. High fluxes could be obtained by pretreating at low pressures (600 to 2 000 kPa). At somewhat higher pressures (4 000 - 6 000 kPa) resulting fluxes were lower, but rejection increased up to 80% from solution at pH 7 and having a conductivity of about 2,3 mS/cm. A total of 5 000 mg/m^2 was sufficient to modify porosity of CARRE Inc. tubes sufficiently to give satisfactory membranes.

The formation of the zirconium membrane at 600 kPa, 2 000 kPa and 6 000 kPa is shown for naked and pretreated porous stainless steel tubes (CARRE Inc.) in Figures 1, 2 and 3 respectively. The pretreated tubes were treated with fumed silica at 600 kPa, 2 000 kPa and 6 000 kPa respectively.

It will be seen that the zirconium membrane was more readily formed on the pretreated tubes. This effect became more marked as pressure of formation was increased.

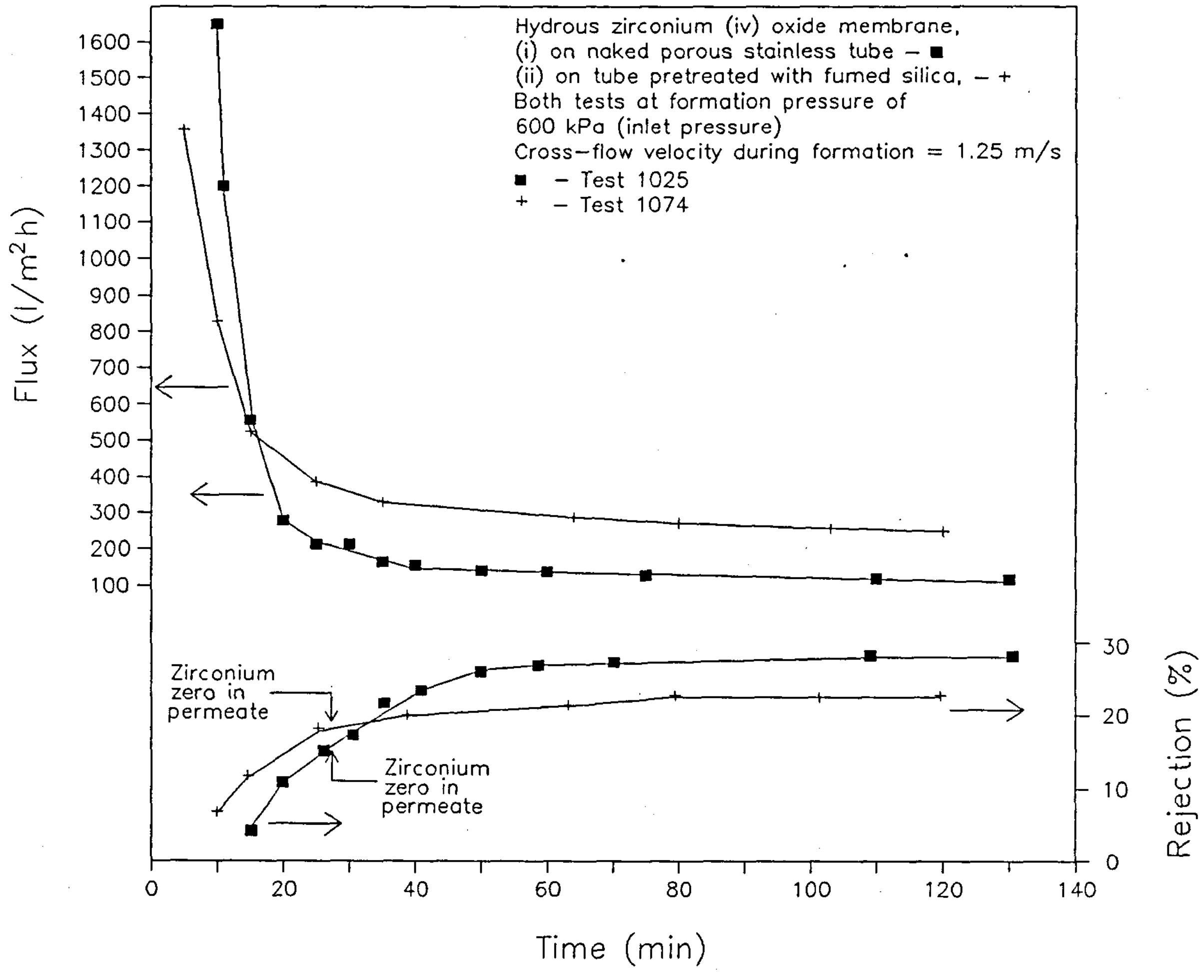

FIGURE 1
Hydrous Zirconium (iv) Oxide Membrane Prepared at 600 kPa

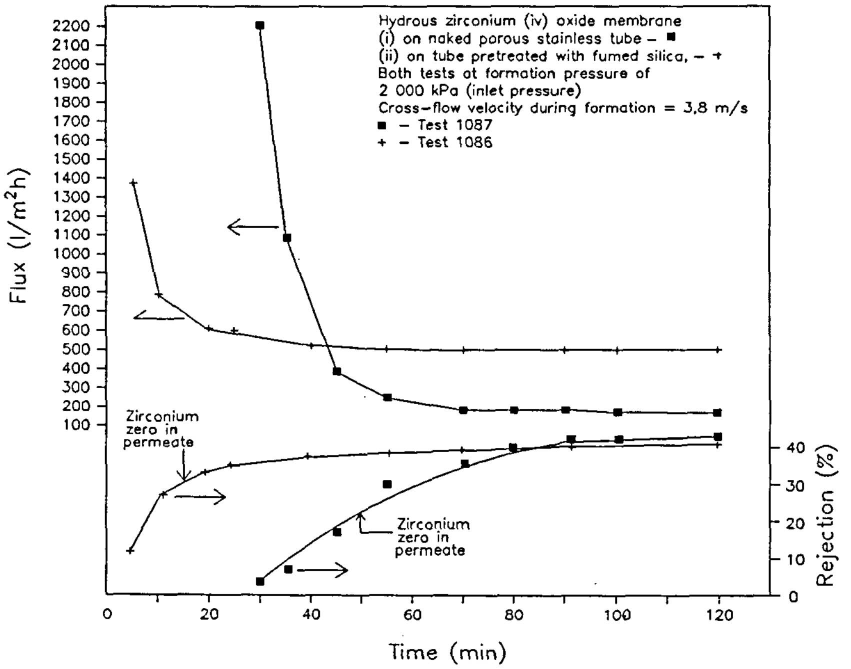

FIGURE 2

Hydrous Zirconium (iv) Oxide Membrane Prepared at 2 000 kPa

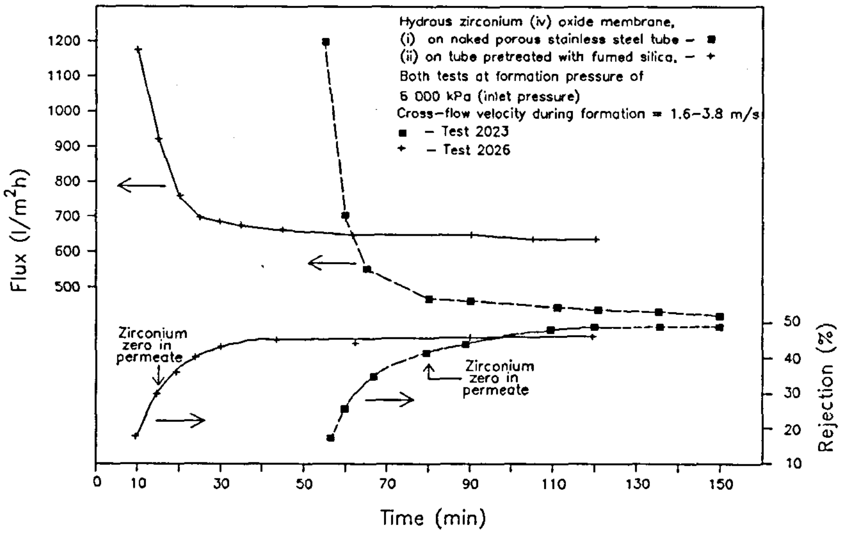

FIGURE 3

Hydrous Zirconium (iv) Oxide Membrane Prepared at 6 000 kPa

1.5 Effect of Storage (Wet)

A number of tubes with Zr/PAA membranes prepared on porous stainless steel tubes (CARRE Inc.), naked and pretreated, was stored under water for varying periods and retested to determine stability. The results of such tests are reflected in Table 3. The composite membranes retained their properties sufficiently well on wet storage.

TABLE 3

Examples of Retesting of Pretreated Tubes After Storage

Test No.	Test pressure kPa	Days stored wet after Zr/PAA formation	Initial results		After storage results	
			Flux ℓ/m^2h	Rejection %	Flux ℓ/m^2h	Rejection %
2039/40 Hydrous zirconia 4 000 kPa Zr, Zr/PAA 6 000 kPa	6 000	9	165	82	186	80
2030/2036 Silica 4 000 kPa Zr, Zr/PAA	6 000	6	240	81	238	81
2029/35 Silica 4 000 kPa Zr/ZrPAA 6 000 kPa	6 000	7	250	80	249	80
2026/27 Silica 6 000 kPa Zr, Zr/PAA 6 000 kPa	6 000	15	230	72	222	75
2023/24 Naked Tube Zr, Zr/PAA 6 000 kPa	6 000	17	87	66	71	80
2019/21 Hydrous zirconia 2 000 kPa Zr, Zr/PAA 6 000 kPa	6 000	23	333	68	294	73
2017/22 Hydrous zirconia 2 000 kPa Zr, Zr/PAA 6 000 kPa	6 000	27	294	67	294	67
2013/2016 Hydrous zirconia 600 kPa Zr, Zr/PAA 600 kPa	6 000	32	366	65	390	63
2041/2043 Hydrous zirconia 4 000 kPa Zr, Zr/PAA 6 000 kPa	6 000	9	195	80	234	78
2044/2046 Hydrous zirconia 4 000 kPa Zr, Zr/PAA 4 000 kPa	6 000	3	264	80	279	80

2 SPECIAL POLYMERS

During 1987 a number of samples of polymers prepared by the Institute for Polymer Science (IPS) (Stellenbosch) were tested and results from IPS, CSIR, and the Pollution Research Group are given in Table 4. Unfortunately no information was given regarding molecular mass or other special properties of the polymers.

TABLE 4

Dynamic Membranes - Comparison of Results on Polymers

Group	Polymers	Robs (%)	Flux ℓ/m²h	pH	Pressure (MPa)	Temp (°C)	Velocity (m/s)	Salt conc. (mg/ℓ)
S	MAVA*1	90	225	7	6	35	6,0	1 770 $NaNO_3$
C		45	315	7	3	30	4,5	2 920 NaCl
P		67	165	8	6	40	5,0	5 000 $NaNO_3$
		78	135	8	6	40	5,0	2 000 $NaNO_3$
S	MAVOH*1	95	132	7	6	35	6,0	2 150 salt
C		53	177	7	3	30	4,5	2 920 NaCl
P		67	38	6,9	6	40	5,0	5 000 $NaNO_3$
		78	34	6,9	6	40	5,0	2 000 $NaNO_3$
S	MAA*1	No results available.						
C	MAA	66	305	7	3	30	4,5	4 250 $NaNO_3$
P		70	144	7	6	40	5,0	5 000 $NaNO_3$
		79	152	6,4	6	40	5,0	2 000 $NaNO_3$
		81	135	8,5	6	40	5,0	2 000 $NaNO_3$
S	AVAC(7)*1	91	320	7	6	-	6,0	2 000 $NaNO_3$
	AVAC(2)*2	94	272	-	6	-	6,0	2 000 $NaNO_3$
C		No results available.						
P	AVAC(7) (received October 1987)	64	114	8,6	6	40	5,0	5 000 $NaNO_3$ + electrolytes from pH adjustment.
		73	177	6,6	6	40	5,0	2 000 $NaNO_3$
S	AVOH(2)*2	99	94	7?	6?	-	6?	2 000 $NaNO_3$
C	AVOH	31	320	7	3	30	4,5	4 250 $NaNO_3$
P	AVOH(7)	56	131	6,5	6	40	5,0	5 000 $NaNO_3$ + electrolytes from pH adjustment
		39	211	6,5	6	40	5,0	2 000 $NaNO_3$

Where:
MAVA - Maleic acid-alt-vinyl acetate
MAVOH - Maleic acid-alt-vinyl alcohol
MAA - Maleic acid-alt-acrylic acid
AVAC - Acrylic acid-co-vinyl acetate
AVOH - Acrylic acid-co-vinyl alcohol.

S - Stellenbosch, (IPS); C - CSIR, NIWR; P - Pollution Research Group.

Under S, *1 results from IPS progress report 1986; *2 results from IPS progress report 3/86.
P results from progress report - Jan-April 1987 and May-Nov 1987 (PRG).
C results from progress report - July-Dec 1986 and Jan-Dec 1987 (CSIR).
Composite table from Addendum to Progress Report for the period January to October 1987.

The results presented by the Pollution Research Group were obtained from membranes prepared on CARRE Inc. porous stainless steel tubes of 0,142 m² area. No pretreatment of tubes was undertaken. Tests were performed only once and results must be viewed with caution. It is not known whether the results by CSIR are on membranes prepared by chelation on a hydrous zirconium (iv) oxide membrane.

In 1988 a sample of unhydrolysed co-polymer of acrylic acid/vinyl acetate and a sample of the 100 % hydrolysed co-polymer were received. These samples were tested on porous stainless steel tubes (0,02 m^2) (CARRE Inc.) which had been pretreated with hydrous zirconia. A comparison was made with the polymer polyacrylic acid (150 000 molecular mass). All tests were carried out on a sodium nitrate containing 2 000 mg/ℓ. The hydrous zirconium oxide membranes were tested at a pH near 3,5 and the composite membranes were tested near pH 7. The results are given in Table 5.

TABLE 5
Comparison Between Composite Membranes, Zr/Polyacrylic Acid and Zr/Polyacrylic Acid - Vinyl Acetate Co-polymer

<table>
<tr><th>Date</th><th>Test</th><th>Membrane</th><th>Porous stainless steel tube no.</th><th>Inlet pressure kPa</th><th>Cross-flow velocity m/s</th><th>Flux ℓ/m²h</th><th>Rejection %</th><th>Conductivity of feed mS/cm</th></tr>
<tr><td>08/11/88</td><td>2042</td><td>Zr</td><td>T4</td><td>6 000</td><td>4,3</td><td>588</td><td>39</td><td>2,46</td></tr>
<tr><td>09/11/88</td><td>2043</td><td>Zr/PAA</td><td>T4</td><td>3 000</td><td>4,6</td><td>75</td><td>70</td><td>2,30</td></tr>
<tr><td>09/11/88</td><td>2043</td><td>Zr/PAA</td><td>T4</td><td>6 000</td><td>4,3</td><td>195</td><td>80</td><td>2,30</td></tr>
<tr><td colspan="9">Tube T4 was pretreated with precipitated hydrous zirconia at 4 000 kPa; Zr and Zr/PAA membranes were formed at 6 000 kPa.</td></tr>
<tr><td>14/11/88</td><td>2045</td><td>Zr</td><td>T1</td><td>4 000</td><td>4,5</td><td>576</td><td>40</td><td>2,68</td></tr>
<tr><td>15/11/88</td><td>2046</td><td>Zr/PAA</td><td>T1</td><td>4 000</td><td>4,4</td><td>159</td><td>78</td><td>2,24</td></tr>
<tr><td></td><td></td><td>Zr/PAA</td><td>T1</td><td>3 000</td><td>4,8</td><td>114</td><td>74</td><td>2,23</td></tr>
<tr><td></td><td></td><td>Zr/PAA</td><td>T1</td><td>6 000</td><td>4,1</td><td>264</td><td>80</td><td>2,23</td></tr>
<tr><td colspan="9">Tube T1 was pretreated with precipitated hydrous zirconia at 4 000 kPa; Zr and Zr/PAA membranes were formed at 4 000 kPa.</td></tr>
<tr><td>29/11/88</td><td>2051</td><td>Zr</td><td>T7</td><td>4 000</td><td>4,5</td><td>636</td><td>41</td><td>2,45</td></tr>
<tr><td>30/11/88</td><td>2052</td><td>Zr/IPS*</td><td>T7</td><td>4 000</td><td>4,5</td><td>105</td><td>85</td><td>2,32</td></tr>
<tr><td></td><td></td><td>Zr/IPS*</td><td>T7</td><td>6 000</td><td>4,3</td><td>165</td><td>88</td><td>2,34</td></tr>
<tr><td colspan="9">Tube T7 was pretreated with precipitated hydrous zirconia at 4 000 kPa; Zr and Zr/IPS membranes were formed at 4 000 kPa.</td></tr>
</table>

* The polymer (co-polymer of polyacrylic acid and vinyl acetate) from the Institute for Polymer Science gave excellent rejection. The flux, however, is somewhat lower than that obtained with Zr/PAA membrane prepared under similar conditions.

The results for the hydrolysed co-polymer are given in Table 6. The composite membrane gave excellent rejection values but the flux was low (see Table 5).

The composite membranes described in Tables 5 and 6 were stored wet and retested after storage. The results are given in Table 7. There was a change in flux and rejection after 30 days wet storage for a Zr/PAA membrane, but the change is not serious. The change in results for the Zr/co-polymer membrane is significant and needs to be examined.

TABLE 6
Test on Composite Membrane Made with Fully Hydrolysed Polyacrylic Acid/Vinyl Acetate Co-polymer

Date	Test	Membrane	Porous SS tube	Inlet pressure kPa	Cross-flow velocity m/s	Flux ℓ/m²h	Rejection %	Conductivity mS/cm
14/12/88	2045	Zr	T9*1	4 000	4,6	519	32	2,47
19/12/88	2055	Zr/IPS*2	T9	4 000	4,4	39	89	2,43
				6 000	4,3	57	90	2,42

*1 Tube was pretreated with precipitated hydrous zirconium at 4 000 kPa; Zr and Zr/polyelectrolyte membrane formed at 4 000 kPa.

*2 Composite membrane; Zr/fully hydrolysed co-polymer.

TABLE 7
Effect of Wet Storage

Date	Test	Membrane	Inlet pressure kPa	Cross-flow velocity m/s	Flux ℓ/m²h	Rejection %	Days storage
19/12/88	2055	Zr/fully hydrolysed co-polymer	6 000	4,3	57	90	initial
22/12/88			6 000	4,4	70	82	after 3 days
30/11/88	2052	Zr/unhydrolysed co-polymer	6 000	4,3	165	88	initial
22/12/88			6 000	4,3	810	23	after 22 days
02/11/88	2040	Zr/PAA	6 000	4,3	165	82	initial
22/12/88			6 000	4,3	222	76	after 50 days

3 USE OF NON-WOVEN POLYETHYLENE-TEREPHTHALATE (PET) TUBES AND PET TUBES COATED WITH POLYETHERSULPHONE POLYMER (PET/PES)

3.1 Characteristics

Both PET and PET/PES tubes were supplied by the Institute for Polymer Science.

Dimensions were as follows:-

	PET tubes	PET/PES tubes
Length	1 050 mm	1 050 mm
Internal diameter	12,9 mm	12,9 mm
Porosity:		
mm Hg for first bubble on propanol wetted tube	23 to 44	390
mm Hg pressure for average emission of bubbles	46 to 48	775 to >1 520

When connected to the cross-flow apparatus, the tubes were protected in a perforated stainless steel outer tube.

3.2 Membranes on PET tubes

Typical results for the PET tubes are given in Tables 8 and 9.

TABLE 8
Flux and Rejection from Naked Tubes on which a Zirconium Membrane had been Deposited at 600 kPa

Test velocity m/s	Flux ℓ/m²h	Robs* %	Test pressure kPa
1,75	49	14,7	600
1,75	76	8	600
1,75	27	26	600
1,75	31	24	600

* 2 000 mg/ℓ $NaNO_3$ solution.

TABLE 9
Flux and Rejection Values Obtained on a Pretreated Tube on which a Zirconium Membrane and Subsequently a Zr/PAA Membrane had been Deposited at 600 kPa (The tube had been pretreated with a dilute suspension of fumed silica)

Test no.	Test velocity m/s	Flux ℓ/m²h	Robs* %	Test pressure kPa	Membrane
2002V	1,75	150	12,5	600	Zr
2003V	1,74	17	36	600	Zr/PAA
	4,70	45	52	2 000	Zr/PAA

* 2 000 mg/ℓ $NaNO_3$ solution.

Although the PET tubes have potential, the tubes have insufficient strength to maintain an undamaged membrane surface at high inlet pressures (above 600 kPa). Pinholing occurred at about 2 000 kPa inlet pressure.

3.3 Use of PET/PES Tubes

A preliminary test on membrane formation on a PET/PES tube was carried out at 600 kPa inlet pressure. Results of this test are given in Table 10.

TABLE 10

Evaluation of Zr and Zr/PAA Membranes Formed on a PET/PES Tube at Low Pressure

Test	Membrane	Evaluation conditions		pH	Rejection	Flux
		Pressure kPa	Cross-flow velocity m/s		(on 2 000 mg/ℓ $NaNO_3$) %	ℓ/m²h
2004 PET/PES	Zr	600	1,75	3,5	20,5	220
	Zr/PAA	600	1,75	6,87	36	50
		3 000	5,30	6,87	31	170
		3 000	3,80	6,87	30	-
		5 000	4,70	6,87	35	-
		6 000	4,80	6,87	36,5	350

Note : Compaction of substrate was evident as pressures were increased.

The substrate did not come up to expectation for low pressure membrane formation. These results were confirmed in further tests.

Three new PET/PES tubes were used to form a hydrous zirconium oxide membrane at low pressure (600 kPa) (pH - 3,5; cross-flow velocity - 1,75 m/s). In all three cases the formation of the membrane with time was identical. The tubes after storage in water were subsequently coated with polyacrylic acid by the standard method also at low pressure. Here again very similar results were obtained. These tubes were then subjected to evaluation at high pressure. A summary of results is given in Table 11.

The Zr/PAA tube (test 2005) immediately after forming at low pressure gave a high rejection at low pressure but failed to yield reasonable rejections at high pressure when tested one day later. When tested again after 6 days storage, results of rejection at low pressure were low (12 %). The composite membrane (Test 2010) failed to perform adequately at high pressure after storage.

The internal surfaces of tubes were examined visually. The original polyethersulphone surfaces were smooth and free from obvious imperfections. Tubes 1, 2 and 3 all showed flawed areas (rough) after testing.

TABLE 11
PET/PES Tubes, Low Pressure Formation of Zr/PAA Membranes

Date	Test	Membrane	Rejection (on 2 000 mg/ℓ $NaNO_3$) %	Flux ℓ/m²h	Cross-flow velocity m/s	Inlet pressure of test (kPa)
06/09/88	2004 PET/PES	Zr Tube 1	20,5	220	1,75	600
07/09/88	2005 PET/PES	Zr/PAA	36	50	1,75	600
08/09/88			31	170	5,30	3 000
08/09/88			36	350	4,80	6 000
14/09/88			12	77	1,75	600
12/09/88	2006 PET/PES	Zr Tube 2	20,2	220	1,75	600
13/09/88	2007 PET/PES	Zr/PAA	38	41	1,75	600
15/09/88	2010 PET/PES	Zr/PAA	5	700	3,6	3 000
14/09/88	2008 PET/PES	Zr Tube 3	20,2	230	1,75	600
16/09/88	2011 PET/PES	Zr/PAA	23	83	1,75	600

Further tests were conducted at formation pressures of 3 000 kPa and 4 000 kPa. The results of such tests are given in Table 12.

TABLE 12
Evaluation of Membranes on PET/PES Tubes, Formed at 3 000 to 4 000 kPa.

Experiment	Membrane	Tube	Inlet pressure kPa	Flux ℓ/m²h	Rejection* %
2016	Zr	PET/PES 4	3 000	608	37
2017	Zr/PAA	PET/PES 4	3 000	92	68 (composite formation)
2017	Zr/PAA	PET/PES 4	6 000	197	77
2017	Zr/PAA	PET/PES 4	800	15	25
2048	Zr	PET/PES 5	4 000	656	46
2049	Zr/PAA	PET/PES 5	4 000	139	80 (composite formation)
2049	Zr/PAA	PET/PES 5	3 000	103	74
2049	Zr/PAA	PET/PES 5	6 000	172	82

* Based on conductivity from a solution containing 2 000 mg/ℓ $NaNO_3$ at pH 3,5 for Zr membrane and 6,5 to 7 for Zr/PAA membrane.

The membranes formed on the PET/PES tubes at higher pressures (3 000 to 4 000 kPa) were satisfactory and responded well to increase in test pressures up to 6 000 kPa.

These tubes were stored wet for extended periods and then re-evaluated. The results are given in Table 13.

TABLE 13

Evaluation of Membranes After Wet Storage

Membrane conditions	Test no.	Test pressure	Cross-flow velocity m/s	Days stored wet after Zr/PAA membrane formation	Initial results		After storage results	
					Flux ℓ/m^2h	Rejection %*	Flux ℓ/m^2h	Rejection %*
Zr, Zr/PAA	2016/2017	6 000	4,5	61	197	77	232	73
3 000 kPa		3 000	4,5		92	68	155	67
Zr, Zr/PAA	2048/2049	6 000	5,1	10	172	82	208	74
4 000 kPa		4 000	5,1		139	80	131	74
		3 000	4,8		103	74	-	-

* Based on conductivity from a solution containing 2 000 mg/ℓ $NaNO_3$ at pH 6,5 to 7.
Both tubes showed satisfactory smooth internal surfaces after tests.

The tubes had shown no deterioration after storage and the inner surface of the tubes remained smooth after the test. Clearly with PET/PES tubes, it is necessary to prepare membranes at pressures above 600 kPa.

4 PORE SIZE OF VARIOUS SUPPORTS

The investigations on pretreatment of tubes has highlighted the importance of pore size on the properties of Zr and Zr/PAA membranes. The thickness of the porous support will also be important.

The porosity of some of the supports which have been used are given in Table 14 in terms of air pressure required to allow bubbles to merge from the porous material wetted with propanol. The results are compared with those obtained with Millipore and Nucleopore membranes. The method was based on an ASTM procedure (5).

From the above it can be seen that the thin Millipore and Nucleopore membranes are extremely uniform (maximum and mean values very similar). The stainless steel tubes vary significantly between each other and uniformity is poor generally. After pretreatment with fumed silica the pore size was improved.

TABLE 14
Porosity of Porous Materials

Support	Air pressure for maximum pore size mm Hg	Air pressure for mean pore size mm Hg
Polyethylene-terephthalate (PET) tubes supplied by the Institute for Polymer Science	23 to 44	46 to 48
PET/PES tubes supplied by the Institute for Polymer Science		
Tube 1	152	980
2	220	775
3	114	1 520
4	342	>1 520
Porous stainless steel (CARRE Inc.)		
Tube a	121	184
b	120	270
c	95	360
d	113	268
e	154	214
f	169	279
g	164	239
h	134	234
Porous stainless steel (CARRE Inc.) naked and pretreated with fumed silica		
T8 untreated	132; 123	271; 252
T8 pretreated	173; 154	320
T7 untreated	208	282; 371
T7 pretreated	294	414
Porous stainless		
Pall	38	68
Framatome	142	208
Krebsöge GMBH		
Cat. No. 9136/10; 1 μ	123	132
Cat. No. 9136; 1 μ	77	111
Cat. No. 9270; 1 μ	102	123
(Sources of supply of stainless steel tubes are given in Appendix 4).		
Commercial membranes		
Millipore - mixed esters of cellulose acetate and nitrate; 0,45 μm	541	586
Nucleopore polycarbonate, 1 μm	414	469

5 CONCLUSIONS - SECTIONS 1 TO 4

5.1 Porous Stainless Steel Tubes

(i) Where porous stainless steel tubes are used as supports for hydrous zirconium oxide membrane or for hydrous zirconium oxide/polyelectrolyte, it is desirable to pretreat the tubes with hydrous metal oxides such as silica and zirconium.

The permeability of the naked tubes determined from the flux of pure water at a given inlet pressure, varies from tube to tube in any given batch. Pore size distribution is poor and in some cases there is a significant difference between maximum and mean pore size. After pretreatment with fumed silica or hydrous zirconia, permeability decreased significantly and permeate emerged evenly over the length of a tube.

(ii) Hydrous zirconium oxide membranes are more readily deposited on the pretreated tubes than on the naked tubes. This effect becomes more marked as pressure of formation is increased. A polyelectrolyte such as polyacrylic acid chelates readily with the zirconium membrane yielding a stable composite membrane.

(iii) A certain amount of tailoring can be undertaken. High fluxes can be obtained by pretreating at low pressure (600 to 2 000 kPa). At somewhat higher pressures (4 000 to 6 000 kPa), the resulting fluxes are low, but the rejection increases.

(iv) After treatment of the porous stainless steel tubes with a suspension of fumed silica or a suspension of precipitated zirconium hydroxide (hydrous zirconia) the tubes can be stored wet before the zirconium and zirconium/polyelectrolyte membranes are formed. No deterioration of pure water permeability was noted.

(v) Composite membranes using polyacrylic acid and prepared on pretreated tubes can be stored wet for long periods without any significant deterioration.

5.2 Non-Woven Fabric Tubes

(i) Polyethylene-terephthalate tubes (PET) (protected in a perforated steel outer tube).

Although these tubes have potential as supports for dynamic membranes, the have insufficient dimensional stability and pinholing is a problem at pressures as low as 2 000 kPa.

(ii) PET tubes which have been internally coated with polyethersulphone (PES) do make satisfactory supports for dynamic membranes formed at pressures above 600 kPa. (These tubes must also be protected in a perforated stainless steel outer tube).

Membranes were unstable after wet storage if formed at low pressure. At a formation pressure of 3 000 kPa, composite membranes with satisfactory wet storage properties were produced.

It is considered that the PET/PES support tubes have considerable potential and detailed investigations on membrane formation and membrane stability and rejection/flux properties should be undertaken.

6 TREATMENT OF EFFLUENT FROM POLYMER MANUFACTURE

6.1 The Effluent

Supacryl (Pty) Ltd. produces polymeric, acrylic and other emulsion polymers at a plant in New Germany, South Africa. Effluent is divided into two streams:-

(i) a weak white-water containing polymers such as acrylics and methacrylics. This stream has a total solids loading of about 1,3 g/ℓ and a volume of 13 to 16 m^3/d.

(ii) a strong white-water with a total solids loading of about 10 g/ℓ and a volume of about 12 m³/d.

Since the polymers are present in colloidal form in the effluent, it was decided to examine the use of an "inert" filter system involving the deposition of a fine suspension of hydrous silica. Also, since the polymers in the white-water effluent could chelate with a zirconium membrane, it was decided to examine the use of composite membranes rather than hydrous zirconium oxide membranes as had been done previously.

6.2 Use of Fumed Silica on Porous Stainless Steel Tubes

It has been shown **(6,7,8)** that a dynamically formed membrane is well suited for the ultrafiltration of emulsions. A dispersion of silica (Cab-O-Sil) was the material used to prepare the membrane. This was essentially the method used for modifying the pore size of porous stainless steel tubes (section 1.2) before application of zirconium or zirconium/polyelectrolyte membrane.

A porous stainless steel tube (CARRE Inc.) was treated with a dispersion of Cab-O-Sil (fumed silica) by passing the dispersion (40 g/100 ℓ) in a cross-flow mode through the tube. The initial water flux for the porous tube was over 33 000 ℓ/m²h at an inlet pressure of 1 000 kPa and cross-flow velocity of 2,5 m/s. After addition of the dispersion to the flow, the flux at 4 000 kPa and cross-flow velocity near 4,3 m/s was decreased over 60 minutes to about 1 250 ℓ/m²h.

The tube was removed from the apparatus and stored in water while the dispersion was replaced with a sample of Supacryl white-water effluent. The tube was then refitted and the effluent passed in cross-flow mode through the silica-treated tube at different inlet pressures as shown in Table 15.

TABLE 15

Treatment of White-water Effluent Using a Silica-treated Porous Stainless Steel Tube

Feed : TC = 1,56 g/ℓ.
Absorbance at 525 nm = 2,75.

Test	Inlet pressure kPa	Cross-flow velocity m/s	Rejection %			Flux ℓ/m²h
			Conductivity	TC	Absorbance at 525 nm	
3001	4 000	4,5	55	97	98	290
	6 000	4,3	59	96	96	330
	3 000	4,6	54	99	98	180

The above results are extremely encouraging. The relatively high conductivity rejection for this membrane is interesting. Tests should now be conducted with porous stainless steel tubes which have been pretreated with precipitated hydrous zirconium oxide since this may make the cleaning operations more simple.

6.3 Dynamic Zirconium/PAA Membrane

A porous stainless steel tube was pretreated with precipitated hydrous zirconium oxide and then coated with a hydrous zirconium oxide membrane followed by chelation with a polyacrylic acid membrane.

The results of tests on white-water effluent using the composite membrane are given in Table 16.

TABLE 16

Treatment of White-water Effluent Using a Composite Zr/PAA Membrane on a Silica Pretreated Porous Stainless Steel Tube

Date	Test	Inlet pressure kPa	Cross-flow velocity m/s	Rejection %			Flux ℓ/m^{2}h
				Conductivity	TC	Absorbance at 525 nm	
15/11/88	2046	3 000	4,8	74	-	-	114
	on 2 000 mg/ℓ	4 000	4,4	78	-	-	159
	$NaNO_3$ soln.	6 000	4,1	80	-	-	264
21/12/88	3002	4 000		76	99	99	116
	on Supacryl	6 000		82	99	99	135
	white-water						

The preliminary results are very encouraging but long term tests are required to determine deterioration of flux for both silica membrane and composite Zr/PAA membrane.

SECTION B : INVESTIGATIONS ON POROUS STAINLESS STEEL TUBES FROM 0,14 m^2 TO FULL-SCALE MODULES UP TO 6,35 m^2

7 THE EFFLUENTS

The current range of effluents for which dynamic membrane technology was recommended are all of a highly fouling nature. The effluents arise from dyehouse effluent from Mym Textiles, wool washery effluent from Gubb & Inggs Ltd. and polymer manufacture at Supacryl (Pty) Ltd.

Effluents from the wool washery are being treated with hydrous zirconium (iv) oxide membranes since fouling, although serious, appears not to be related to reaction of constituents of the effluent with the membrane.

Effluents from polymer manufacture may well contain constituents that could react with the hydrous zirconium (iv) oxide layer, and it would therefore be reasonable to protect the zirconium membrane by chelation with a known polymer rather than to allow reaction to occur randomly between the polymer constituents of the waste-water and the zirconium membrane. Alternatively, consideration should be given to the use of a silica or other hydrous metal oxide type dynamic membrane (section 6.2).

The highly complex mixture of chemicals, including classes and varieties of dyes from a dye-house effluent, suggests that a composite membrane is likely to give better long term service than a highly reactive hydrous zirconium (iv) membrane and investigations on the effluent were confined to the use of the composite membrane.

Preliminary investigations at three factory sites are described in the following sections. More detailed investigations will be carried out in 1989 on a separate project. A paper describing the potential of dynamic membranes for the treatment of industrial effluents was presented at the 5th National Meeting of the SAIChE, 15-16 August 1988 (9) and is attached as Appendix 3 A paper on treatment of wool scouring effluents (10) is given in Appendix 4

7.1 The Factories

7.1.1 Mym Textiles

7.1.1.1 Introduction and technical evaluation

During 1984 an effluent treatment plant was installed at Mym Textiles at Umzinto, Natal. The plant was installed to treat the effluent that resulted from the scouring, dyeing and finishing operations. The plant was a reverse osmosis unit using dynamically formed membranes of the zirconium type formed on porous stainless steel supports. (Originally 42 modules of 6,35 m^2 each were available; only 36 modules are now available).

Since the commissioning of the plant there have been numerous problems and the plant has never performed to design specifications, and was later used to treat a common effluent from the dyeing operation. It should be noted, however, that no pilot studies were undertaken. At the beginning of 1988, the performance of the plant had deteriorated to a point at which the continued economic operation of the plant was debatable. At this stage the factory authorities called in the assistance of the Pollution Research Group to undertake a technical evaluation of the plant. This evaluation is covered in Appendix 5 Technical performance evaluation of the dynamic membrane filtration plant at Mym Textiles, Umzinto, February 1988.

7.1.1.2 The problems and changes made to effect improvement

The problems on the plant appeared to be two-fold; corrosion of the u-bends and stand pipes connecting the porous stainless steel elements, and severe fouling of the membranes. The precise nature of the fouling has not been identified, but low cross-flow velocities are thought to have contributed to the fouling.

As a result of the evaluation report, plant management requested a visit to the Gubb & Inggs Ltd. plant at Uitenhage to examine the "open-trough" arrangement of modules. After the visit, Mym Textiles decided to adopt a short term plant for the refurbishing of a section of their membrane plant (Appendix 6).

The refurbishing involved replacing all the u-bends on the porous steel modules with 316 grade stainless steel, placing the modules in open stainless steel troughs in order to facilitate regular inspection and cleaning and finally to re-membrane the plant with dual layer hydrous zirconium oxide/polyacrylic acid type membranes. Such membranes have been judged to produce permeate of acceptable quality during plant trials. The preliminary work involving cleaning/stripping of the porous tubes and experimental membraning on the cleaned naked tubes is given elsewhere (11).

An important aspect that came to light during this work was that high temperature operation can detrimentally affect the colour rejection capability of the membrane. This would be related to the class of dye used.

7.1.1.3 Preparation of membranes for plant operation

Membrane formation was accomplished using the technique recently developed by the Pollution Research Group, whereby the porous stainless steel tubes are precoated with a precipitated hydrous zirconia. After pretreatment in this manner, a hydrous zirconium (iv) oxide membrane followed by a polyacrylic acid type membrane is formed using standard procedures. This results in a membrane with good rejection characteristics and higher fluxes than the membranes produced using the standard technique. Characteristics of the membranes produced at 3 000 kPa and a cross-flow velocity of about 1,8 m/s gave flux values between 80 to 100 ℓ/m^2h and conductivity rejection values between 55 to 75 % from feed solutions of conductivity of 4 mS/cm.

Membrane formation was completed by the end of 1988. Performance figures and other relevant information will be shown in reports generated by the new project for 1989 entitled "Technical Support for the Application of Dynamic Membrane Plants for the Treatment of Industrial Effluents".

7.1.2 Gubb & Inggs Ltd.

Work at this factory has been carried out under the project "Research into the Treatment of Wool Scouring Effluents".

For this effluent a zirconium membrane appears to be adequate and this membrane is being applied to pretreated stainless steel tubes. (Ten modules of 6,35 m^2 are available).

7.1.3 Supacryl (Pty) Ltd.

Supacryl (Pty) Ltd., which used to be the South African subsidiary of Rohm & Haas (SA) (Pty) Ltd., had problems in discharging emulsion polymerisation wash water to the municipal sewer because of the foaming nature of the effluent. As a result of limited tests undertaken by the Pollution Research Group in 1982, the parent company financed the installation of an automated pilot plant in 1985 consisting of two modules of CARRE Inc. tubes (6,35 m^2 and 2,16 m^2 respectively).

The effluent, which results from the high pressure water cleaning of the polymer reaction vessels is milky in colour, has a high total organic content and contains a foaming agent. The effluent is referred to as white-water effluent (WWE). Present in the effluent are a considerable number of polymers and co-polymers and limited quantities (parts per million) of some monomers and short chain polymers.

Some of these polymeric species undoubtedly react with hydrous zirconium (iv) oxide membrane and a secondary membrane is formed. Although this secondary membrane has no detrimental effect with regard to rejection of colloids and other carbon components, it does reduce the flux considerably.

These randomly and fortuitously formed secondary membranes were exceptionally difficult to clean or strip. The fouled porous tube bundles were removed from their shrouds and each individual bundle was treated with sodium hydroxide solution and hydrogen peroxide as described elsewhere **(10)**.

The difficulties in stripping prompted the decision to form a composite membrane from a known polymer, such as polyacrylic acid of known molecular mass. It is considered that the advantage of this type of membrane would be that the active sites present on the hydrous zirconium (iv) membrane will be taken up by the polyacrylic acid. The result would be a membrane that would be more inert with regard to reaction with random species present in the effluent.

The above effects are demonstrated in Figures 4 to 5. The zirconium membrane had a high rate of flux decline and as the secondary membrane formed, the total carbon

(TOC) rejection increased whereas with the composite membranes flux declined slowly and rejection remained high. An added advantage of a composite membrane would be a higher ionic and organic carbon rejection.

Some preliminary tests on various samples of white-water and using 0,14 m^2 tubes have been done on the use of composite membranes. These membranes were prepared on naked stainless steel tubes **(11)**. Good rejection of total carbon was achieved. It is anticipated, however, that when composite membranes are prepared on tubes pretreated for pore size modification, better flux values will be achieved (see sections 6.2 and 6.3). The use of pretreated tubes only, that is, without a composite membrane, will have to be undertaken concomitantly.

Such work will be required to be done now under the project "Technical Support for the Application of Dynamic Membrane Plants for the Treatment of Industrial Effluents" in 1989.

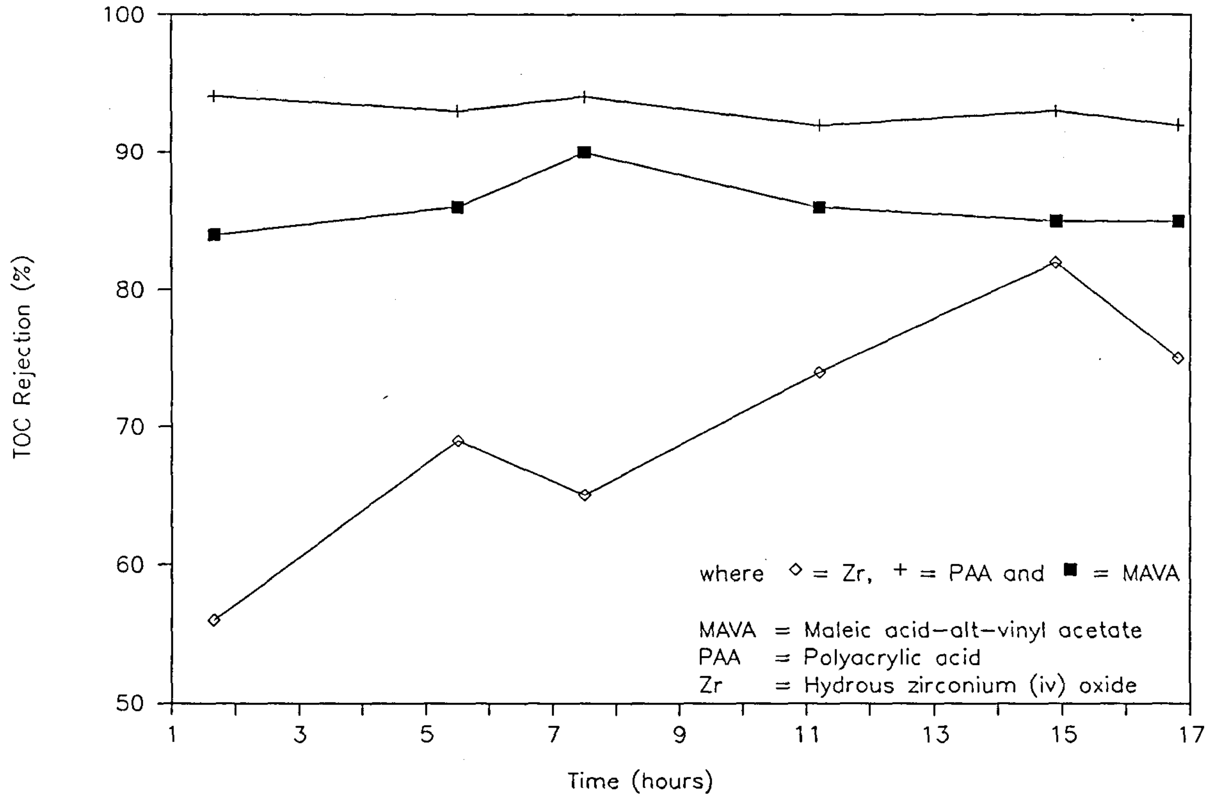

FIGURE 4
Time Versus TOC Rejection (White-water Effluent)

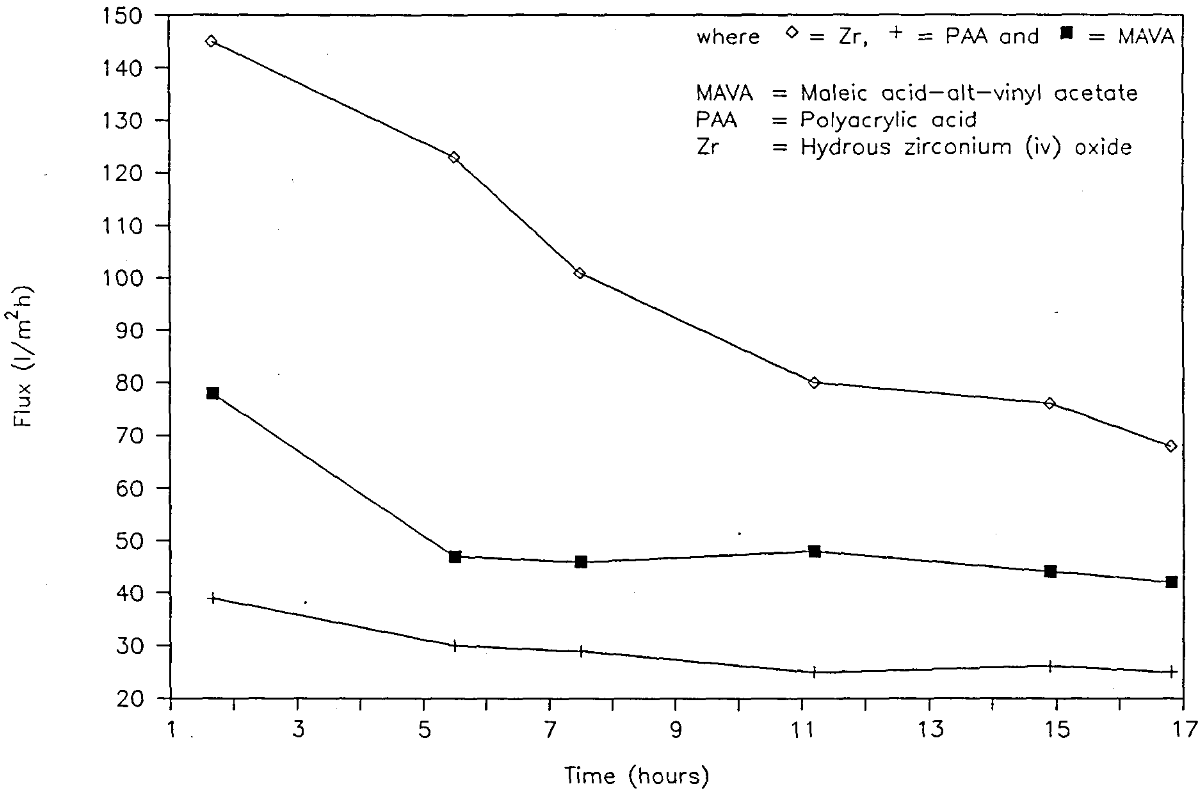

FIGURE 5
Time Versus Flux (White-water Effluent)

8 CONCLUSIONS AND RECOMMENDATIONS

8.1 Section A

(i) CARRE Inc. porous stainless steel tubes have a non-homogeneous pore size distribution and in many cases there is a significant difference between maximum and mean pore size.

If such tubes are treated with suspensions of hydrated silica (Cab-O-Sil) or precipitated hydrated zirconium oxide, the pore sizes are modified leading to a more even distribution of pore size.

(ii) Hydrous zirconium (iv) oxide membranes are more readily deposited on the pretreated tubes than on the naked tubes. This effect becomes more marked as pressure is increased. A suitable polyelectrolyte reacts readily with the zirconium membrane to yield a stable composite membrane.

(iii) A certain amount of tailoring can be undertaken. High fluxes can be obtained by pretreating at low pressures (600 to 2 000 kPa) and evaluating at high pressure (6 000 kPa). At somewhat higher formation pressures (4 000 to 6 000 kPa) resulting fluxes are lower, but the rejection higher at an evaluation pressure of 6 000 kPa.

(iv) Composite membranes, using polyacrylic acid and prepared on pretreated stainless steel tubes (CARRE Inc.) can be stored wet for long periods without significant deterioration.

(v) Porous stainless steel tubes (CARRE Inc.) coated with a silica suspension (Cab-O-Sil), have been shown to be effective in treating white-water effluent from a polymer manufacturing process. This finding needs to be followed up in greater detail.

(vi) Two polymers from the Institute for Polymer Science (polyacrylic acid - vinyl acetate co-polymer and the corresponding fully hydrolysed co-polymer) were used to prepare composite membranes on pretreated porous stainless steel tubes (CARRE Inc.).

Excellent ionic rejection values (88 to 90 %) compared to 80 % for a polyacrylic composite membrane were obtained. Flux values were, however, lower and wet storage appeared to be poor. This aspect needs follow up.

(vii) Polyethylene-terephthalate tubes (PET) have potential as support for dynamic membranes but the tubes as supplied by the Institute for Polymer Science had insufficient dimensional stability. Pinholing was a problem at pressures as low as 2 000 kPa.

(viii) PET tubes which have been internally coated with polyethersulphone (PET/PES) do make satisfactory supports for dynamic membranes prepared at pressures above 600 kPa. At low formation pressure the dynamic membranes were unstable after wet storage. At formation pressure of 3 000 kPa, composite membranes with satisfactory wet storage properties were produced.

It is considered that the PET/PES support tubes have considerable potential and detailed investigations on membrane formation and membrane stability and rejection/flux properties should be undertaken.

8.2 Section B

(i) Progress has been made in the examination of, and improvement in, the application of dynamic membranes at Mym Textiles. Composite membranes (Zr/PAA) have been prepared on pretreated tubes and initial results are good.

(ii) At Gubb & Inggs Ltd. hydrous zirconium (iv) oxide membranes have been prepared on pretreated tubes and initial results are good.

(iii) Work at Supacryl (Pty) Ltd. has been confined to stripping and cleaning of badly fouled modules and some laboratory trials. Such laboratory tests have indicated that work should proceed with composite membranes rather than the zirconium membrane. Such membranes should be prepared on pretreated tubes. Concomitantly, work needs to be done on the use of porous tubes treated with hydrous oxides such as silica, but without any zirconium or zirconium/PAA membrane.

(iv) Work described in (ix), (x) and (xi) should be continued under the project "Technical Support for the Application of Dynamic Membrane Plants for the Treatment of Industrial Effluents".

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APPENDIX 1

EXTENDED ABSTRACT

DYNAMICALLY FORMED HYDROUS ZIRCONIUM (IV) OXIDE/POLYACRYLIC MEMBRANES; LOW PRESSURE FORMATION, HIGH PRESSURE EVALUATION

International Membrane Technology Conference,

Sydney, Australia, November 1988

Pollution Research Group
Department of Chemical Engineering
University of Natal
Durban

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Extended Abstract

DYNAMICALLY FORMED HYDROUS ZIRCONIUM (IV) OXIDE/POLYACRYLIC MEMBRANES; LOW PRESSURE FORMATION, HIGH PRESSURE EVALUATION

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INTRODUCTION

Dynamic membranes are formed *in situ* when a dilute solution (colloidal) of one or more specific additives is passed over the surface of a porous support. Zirconium (iv) species are polymerized in aqueous solutions and polymerization increases with decreasing acidity. At concentrations as low as 10^{-4} molar zirconium, a colloid phase exists even at low pH values. This colloidal condition is important in the formation of a hydrous zirconium (iv) oxide membrane on a porous support by cross-flow techniques (Zr membrane).

The ability of zirconium to react strongly with oxygen containing species is another important property leading to the chelation of polyelectrolytes such as polyacrylic acid onto a preformed hydrous zirconium (iv) oxide membrane, and so producing a composite membrane (Zr/PAA membrane). This chelation tends to occur most easily between five- and six-membered rings and transition metals, since bond distortion occurs least frequently in such rings.

It has been proposed that when a dilute colloidal suspension of hydrous zirconium (iv) oxide is passed across the surface of a porous substrate, the first stage of membrane formation involves "pore filling" or "bridging" stage where colloidal particles of hydrous zirconium oxide are captured on the walls of the pores of the support material. This process causes the pores to close after a period and is followed by the formation of a surface filtration "cake" from colloidal particles, as commonly occurs in other types of cross-flow filtration. This then represents the hydrous zirconium (iv) oxide membrane, which in acid solutions is an anion exchanger.

When a polyelectrolyte such as polyacrylic acid (PAA) is then passed over the hydrous zirconium (iv) oxide, the electrolyte enters the pores of the membrane rather than forming a gel on the surface. It is also suggested that at low pH values the polyelectrolyte molecules are hypercoiled and easily able to penetrate the hydrous zirconium oxide substrate and react with the substrate at this pH. If the pH is then raised, the polyelectrolyte molecules ionise and expand to block the pores, thereby causing a rapid decrease in flux and an increase in rejection. The membrane so formed represents the composite membrane (Zr/polyelectrolyte) which in neutral to alkali solutions has the properties of a cation exchanger.

SELECTION OF POROUS SUPPORT

In this investigation, porous stainless steel supports have been selected as the main support medium. High pressure operation is possible with robust stainless steel supports and this enables single tapered operation without the need for recycle.

Most techniques for membrane preparation involve formation at high pressure and high cross-flow velocity, typically 6 000 kPa and 6 m/s respectively.

Since the advantages of low pressure membrane formation are real, it was decided to examine low pressure membrane formation and high pressure evaluation of composite membranes formed on porous stainless steel supports.

EXPERIMENTAL

Apparatus

A small 50 ℓ cross-flow rig using a Hydra-Cell D10 pump was used in experiments at low pressure (600 kPa) and a second cross-flow rig (100 ℓ) using four D10 pumps in parallel was used for experiments above 600 kPa to 6 000 kPa.

The porous stainless steel tube dimensions were: internal diameter, 14 mm; external diameter, 21.3 mm; effective porous length, 455 mm; effective internal area, 0.02 m^2. Pore size, determined by a modified ASTM procedure, ranged from 2 to 7 micron.

Method of Formation

A standard method of formation similar to that developed at Oak Ridge National Laboratory, USA, was used. Tests were carried out at 40°C (unless stated otherwise).

RESULTS

A series of tests was carried out in which the pressure, cross-flow velocity and pH were varied; pressure from 100 to 600 kPa; cross-flow velocity from 0.1 to 1.25 m/s, pH 2.6 - 3.9. Membranes, which could also be used at high pressure, were produced when formation conditions were, pressure above 300 kPa and pH above 3. Cross-flow velocity did not appear to have a significant influence over the range used.

The results of typical membranes formed from an initial hydrous zirconium (iv) oxide suspension containing 10 mg/ℓ Zr at pH 3.5, at an inlet pressure of 600 kPa and at a cross-flow velocity of 1.25 m/s are shown below.

	Formation		Evaluation at high pressure			
Inlet pressure, kPa	600		3 000		6 000	
Cross-flow velocity, m/s	1.25		approx. 4		approx. 4	
Flux, ℓ/m^2h	28	32	90	87	165	180
Rejection, %*	31	38	66	67	69	67

* from 2 000 mg/ℓ $NaNO_3$ solution.

Membraning of large porous stainless steel modules (Carre Inc.), using the same type of porous stainless steel, was carried out at high pressure (6 000 kPa inlet pressure) at the same time as the low pressure tests were in progress. The total area of a complete module was 6.35 m^2 with a total support length of 134.5 m.

A typical composite membrane formed on such tubes gave a rejection of 73% and a flux of 80 ℓ/m^2h at a pressure 6 000 kPa and a cross-flow velocity of about 5 m/s.

There did appear to be a variation in flux and rejection for some of the membranes prepared on the porous stainless steel supports. It was considered that this might be due to the large variation in pore size and materials were examined for pore size modification. It was decided to use fumed silica and a product called Cab-O-Sil, M.5 produced by Cabot Corp. was selected. The material has a surface area of 200 - 400 m^2/g and a nominal particle size (diameter in microns) of 0.007 - 0.014.

THE PRETREATMENT PROCEDURE

A two gram sample of Cab-O-Sil was carefully creamed, diluted to about 200 mℓ and subjected to agitation with a high frequency vibratory agitator. The well dispersed concentrate was further diluted to 1 000 mℓ and again agitated. A suitable aliquot portion of the stable suspension was then added to the feed tank of the cross-flow rig giving a 2 mg/ℓ silica suspension.

The suspension was passed through the naked porous stainless steel tubes at a selected cross-flow velocity and at a selected inlet pressure until the flux settled down to a steady value, usually after one hour.

Tubes were coated with the silica at a cross-flow velocity of 1.25 m/s and an inlet pressure of 600 kPa. A zirconium membrane was then deposited in the usual manner, followed by chelation with polyacrylic acid to a form a composite membrane. The composite membrane was evaluated at 3 000 and 6 000 kPa.

Characteristics of Membranes Formed on Pretreated Tubes

	Test	Membrane	Cross-flow velocity m/s	Pressure kPa	Flux ℓ/m^2h	Rejection % (2 000 mg/ℓ $NaNO_3$)
Formation - low pressure	35	Zr	1.25	600	201	29
	36	Zr	1.25	600	252	24
	35/1	Zr/PAA	1.25	600	56	34
	36/1	Zr/PAA	1.25	600	62	34
Evaluation - high pressure	35/2	Zr/PAA	4.9	3 000	216	56
			4.3	6 000	522	56
	36/2	Zr/PAA	4.4	3 000	237	58
			4.3	6 000	503	59

The high permeate flux caused polarisation and high cross-flow velocities were thus required to overcome this at the high pressure used in evaluation.

Membrane formation was examined at somewhat higher pressure, 2 000 kPa and the characteristics of such a membrane at high pressure are compared with a membrane formed on a naked tube at 2 000 kPa and with a membrane formed on a pretreated tube at 600 kPa.

Evaluation of Membranes at 6 000 kPa

	Composite membrane formed at 600 kPa	Composite membrane formed at 2 000 kPa	Composite membrane formed at 2 000 kPa
	(pretreated tube)	(pretreated tube)	(naked tube)
Flux, ℓm^2h	522	588	111
Rejection, %*	56	67	55
Cross-flow velocity, m/s	4.3	4.2	3.9

* from 2 000 mg/ℓ $NaNO_3$ solution.

The membranes on pretreated tubes give extremely good flux values; the rejection and flux values are better at the higher formation pressure (2 000 kPa) and far superior to values obtained on the naked tube.

When the fumed silica was added to the feed containing the hydrous zirconium (iv) oxide, it was found that the membranes formed were no better than those formed in the absence of silica.

CONCLUSIONS

The results have demonstrated the remarkable ability of the colloidally dispersed zirconium (iv) oxide to "pore fill" and bridge the large pore sizes present in the tubes used in the tests. Some prior "pore filling" with a larger sized colloidally dispersed silica at very low concentrations (2 mg/ℓ) improved the reproducibility of the results and assisted in producing a high flux membrane which can be formed at low pressure and subsequently used at high pressure.

Further work in this field is necessary to examine the optimum formation pressure.

F.G. Neytzell-de Wilde
August 1988

APPENDIX 2

DYNAMICALLY FORMED HYDROUS ZIRCONIUM (IV) OXIDE/POLYACRYLIC MEMBRANES; LOW PRESSURE FORMATION, HIGH PRESSURE EVALUATION

Contribution to the Workshop on Desalination and Membrane Processes,

Ohrigstad, 24-26 August 1988

Pollution Research Group
Department of Chemical Engineering
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SUMMARY

Dynamic membranes are formed *in situ* when a dilute solution of one or more specific additives is passed over the surface of a porous support. Zirconium (iv) species are polymerised in aqueous solution and polymerisation increases with decreasing acidity. At concentrations as low as 10^{-4} molar zirconium, a colloid phase exists even at low pH values (pH 3). This colloidal condition is important in the formation of a membrane on a porous support by cross-flow techniques.

The ability of zirconium to react strongly with oxygen containing species is another important property leading to the chelation of polyelectrolytes such as polyacrylic acid onto a preformed hydrous zirconium (iv) oxide membrane, and so producing a composite membrane.

In this investigation porous stainless steel supports have been selected as the main support medium. The pore size in the supports varied from 2.0 to 7.0 microns. Tests were carried out in forming membranes at low pressures, (<600, 600 and 2 000 kPa) and evaluating such membranes at high pressures up to 6 000 kPa. This enabled comparison with similar membranes formed at high pressure (6 000 kPa).

A standard method of formation, similar to that developed at Oak Ridge National Laboratory, USA, was used.

It was found that the low pressure technique (600 kPa) for dynamic membranes of the zirconium/polyelectrolyte type resulted in satisfactory membranes when compared to those prepared at high pressure (6 000 kPa).

There was, however, some variation in flux and rejection of the membranes. This may have been related to the large pore size of the tubes used. Tests were therefore, carried out on pretreating the tubes with a suspension of fumed silica. The degree of reproducibility of results at formation pressure (600 kPa) improved markedly yielding membranes with high flux and good rejection. When these tubes were operated at higher pressure (6 000 kPa), the high permeate flux resulted in polarisation and high cross-flow velocities were required to obtain good rejection.

INTRODUCTION

Dynamically formed membranes were first produced by a research group at Oak Ridge National Laboratory (ORNL) in America. Such membranes are formed *in situ* when a dilute solution (10^{-4} molar) of one or more specific additives is passed over the surface of a porous support (ref. 1).

The most promising membranes which have been developed are the hydrous zirconium (iv) oxide membrane and the hydrous zirconium (iv) oxide/polyacrylic acid dual layer or composite membrane (refs. 1,2).

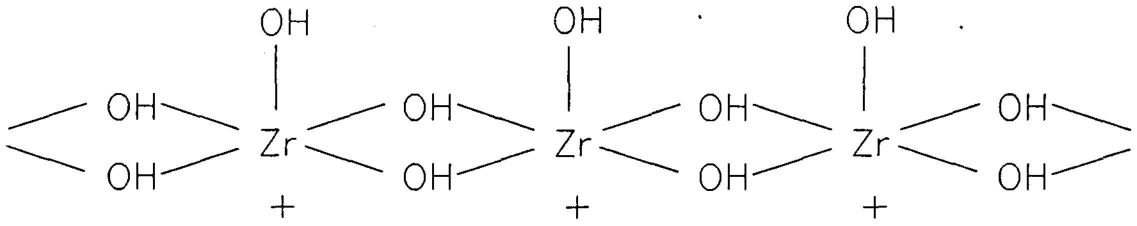
This paper describes investigations involving dynamic hydrous zirconium (iv) oxide membranes formed from a zirconium nitrate membraning solution. In using porous stainless steel supports, nitrate salts were selected to avoid serious pitting corrosion on the stainless steel in the presence of halide and certain other ions. Composite membranes were formed using polyacrylic acid (PAA) with a molecular mass of about 150 000 daltons.

Some Aspects of the Chemistry Involved

Zirconium and hafnium always occur together in nature and because they have very similar properties, their separation is both difficult and expensive. Thus, for most practical applications, other than in atomic energy generation, the hafnium is not separated from the zirconium (ref. 3). The zirconium nitrate solutions were prepared from zirconium basic carbonate by treatment with 93 to 95% nitric acid. The resulting zirconium nitrate salt would contain about 2% hafnium (HfO_2).

Zirconium (iv) species are polymerized in aqueous solutions and studies are complicated by the sensitivity of the species to their environment and the slowness with which the systems attain equilibrium (ref. 4). The increasing polymerisation with decreasing acidity can be followed readily by light scattering studies. Using simple Tyndallometric tests and dilute solutions of zirconium oxychloride or nitrate, it can be shown that at concentrations from as low as 10^{-4} molar zirconium, a colloid phase exists at pH values as low as 3.0. Once formed, the colloid will not readily revert to the soluble form even when the pH is reduced to 2.0. However, hydrous zirconium (iv) oxide will dissolve slowly in nitric acid as solutions increase in molarity from 0.1 molar. At 0.5 molar, solution is quite rapid.

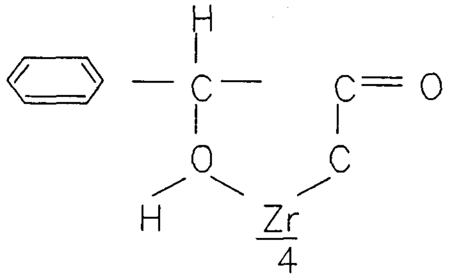
The zirconium polynuclear hydroxy species can be cationic, anionic or neutral. The hydroxy nitrate is cationic:



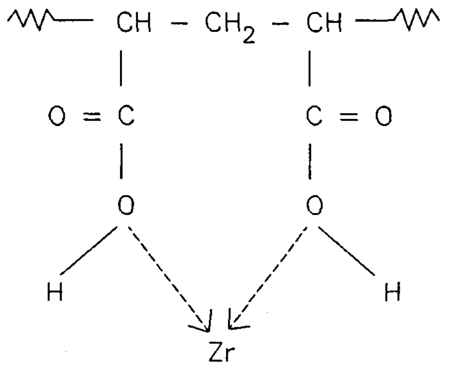
The nitrate ion is not bonded to the zirconium and the remainder of the co-ordination sphere is made up with water to give a co-ordination number of eight for zirconium. Anionic species of zirconium are characterised by the sulphates or carbonates whereas the acetate polymeric material is neutral.

The ability of zirconium to react strongly with oxygen-containing species has led to the increasing use of zirconium-organic polymer systems. At least two -OH groups or at least one (-CO-) radical as an aldehyde or carbonyl group or polypeptide link (-CO-NH-) should be present.

The organic reagent used in analysis of zirconium is mandelic acid (phenylglycolic acid) and four glycolate groups combine with the zirconium:



A well known chelate complex of zirconium and polyacrylic acid may be shown as follows:



This reaction was used in forming the classic dual layer or composite dynamic membrane (ref. 2).

Chelation tends to occur most easily between five- and six-membered rings and transition metals, since bond distortion occurs least frequently in such rings. Dowler (ref. 5) examined the use of polymers containing the maleic acid group. Here also, the maleic groups not involved in chelation would be partly ionized at neutral pH, producing negatively charged membranes having salt rejecting properties.

A series of homo- and co-polymers (ref. 6) based on the following monomers were tested for dynamic membrane formation with hydrous zirconium (iv) oxide: 2 propenoic acid, 2 methyl-2-propenoic acid, methylene butanedioic acid, ethenyl acetate and ethylene sulphonic acid. Both Dowler and van Reenen used "Millipore" filter substrates.

Now although the zirconium atom has a strong tendency to be complexed by various oxygen containing organic groups, such as the carboxylate group, this formation depends on the absence or presence of other anions in the system. Such anions include sulphate and fluoride as inorganic ions, and a number of organic ions such as oxalate. In the work described in this paper, therefore, during hydrous zirconium (iv) oxide hydroxide formation and during zirconium/organic complex formation, the aqueous systems contained nitrate rather than other ions.

Model for Formation

It has been proposed that when a dilute colloidal suspension of hydrous zirconium (iv) oxide is passed across the surface of a porous substrate, the first stage of membrane formation involves a "pore filling" or bridging stage, where colloidal particles of hydrous zirconium (iv) oxide are captured on the walls of the pores of the support material. This process causes the pores to close after a period and is followed by the formation of a surface filtration "cake" from colloidal particles, as commonly occurs in other types of cross-flow filtration. This then represents the hydrous zirconium (iv) oxide membrane, which in acid solutions is an anion exchanger.

When a polyelectrolyte such as polyacrylic acid is then passed over the hydrous zirconium (iv) oxide, the electrolyte enters the pores of the membrane rather than forming a gel layer on the surface. It is also suggested that at low pH values, the polyelectrolyte molecules are hypercoiled and easily able to penetrate the hydrous zirconium (iv) oxide substrate and react with the substrate at this pH.

If the pH is then raised, the polyelectrolyte molecules ionise and expand to block the pores thereby causing a rapid decrease in flux and an increase in rejection (refs. 7,8). The membrane so formed represents the composite membrane (Zr/polyelectrolyte) which in neutral to alkali solutions has the properties of a cation exchanger.

The hydrous zirconium (iv) oxide membranes are characterised by high water fluxes while showing a significant salt rejection. The composite Zr/polyelectrolyte membranes have lower water fluxes but significantly higher salt rejection capability. Actual values will depend on substrate and formation conditions of either the simple or the composite membrane.

To distinguish these membranes from conventional detachable films prepared by casting or other procedures, the class is designated "dynamically formed" or "dynamic".

Selection of Porous Support

In this investigation, porous stainless steel supports have been selected as the main support medium. In industrial applications on the treatment of effluent by membrane techniques, very high pressure operation is possible with robust porous stainless steel supports and this enables single tapered operation without the need for recycle. With long tubes, however, the pressure drop is significant and module design and configuration becomes important (refs. 9,10,11).

Most techniques for membrane preparation involve formation at high pressure and high velocity, typically 6 000 kPa and 6 m/s respectively. Some work, however, has been done in forming composite membranes at pressures from 600 kPa to 6 000 kPa and then evaluating the final membrane characteristics at 6 000 kPa (ref. 2). In these tests, high flux was observed for membranes formed at the lower pressures. As formation pressures increased, flux decreased and final membrane rejection increased. The tests were carried out on "Acropor" and "Millipore" supports.

Working with ceramic tubes of pore size 0.5 to 1 micron at low pressure (800 kPa), Nakao *et. al.* (ref. 12) demonstrated that dynamic ultrafiltration membranes were formed on the porous tubes by filtering colloidal solutions of Zr(iv). The Zr(iv) colloid particles not only deposited on, but also penetrated into the ceramic support. No evaluation tests were done at high pressures.

Since the advantages of low pressure membrane formation are real, it was decided to examine low pressure membrane formation and high pressure evaluation of composite membranes formed on porous stainless steel supports.

EXPERIMENTAL

Apparatus

A small rig using a Hydra-Cell D10 pump, regulated by an electronic speed controller was assembled for tests on rigid supports such as porous stainless steel tubes, or on non-rigid supports such as tubes fabricated from "Viledon", a non-woven fabric or on woven fabric tubes.

A schematic diagram of the rig is given in Fig. 1. Stainless steel (316) was used wherever possible. Teflon flexible hose was used in the line between the pump outlet and the cross-flow support.

Porous Stainless Steel Supports

The tube dimensions were:

internal diameter : 14 mm
external diameter : 21.3 mm
effective (porous) length : 455 mm
effective internal area : 0.02 m^2.

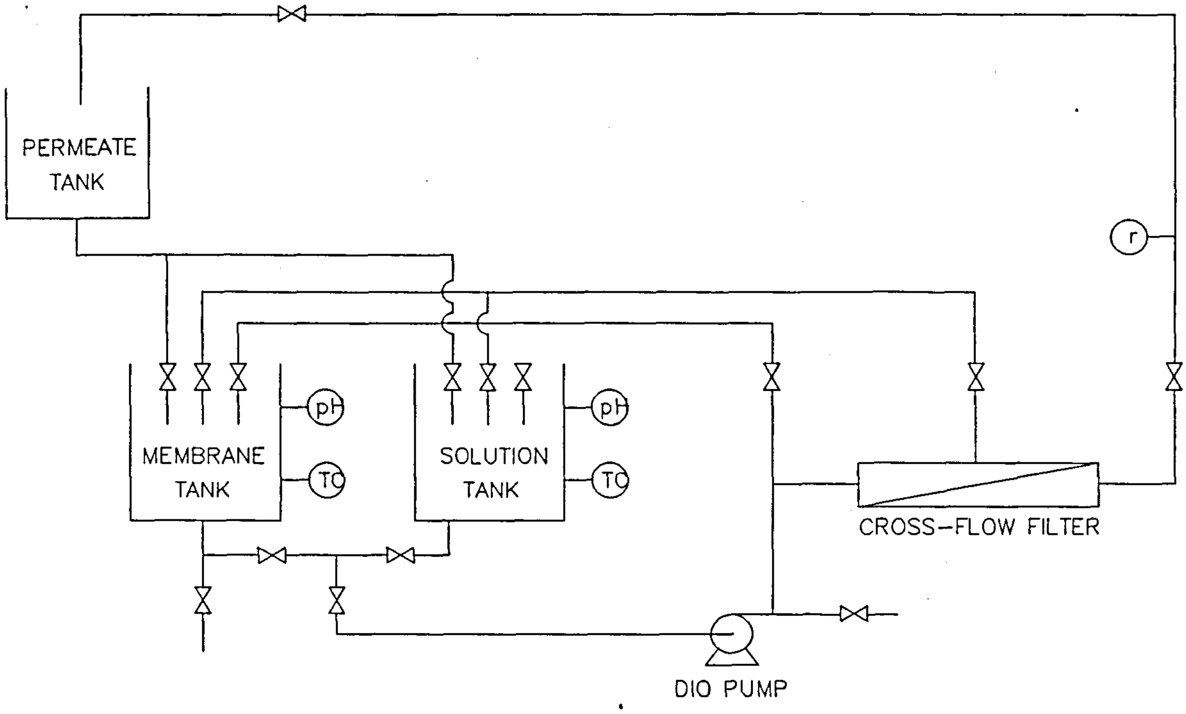


Fig. 1. Low Pressure Cross-flow Rig

A similar cross-flow rig equipped with two or four D-10 pumps in parallel was used for tests at high pressure and high cross-flow velocity.

Ten tubes from a batch were used in the tests described. The pore size was determined using a method based on the ASTM procedure for determining maximum pore diameter (ref. 13). It was found that pore sizes on the naked tubes ranged from 2 micron to 7 micron.

Permeability, determined from the flux of pure water at 600 kPa also varied from tube to tube but in general, was above 25 000 ℓ/m^2h. This variation is unfortunate and must be considered in interpreting the results of the tests undertaken. No attempt was made initially to modify permeability/pore size by depositing additives such as clay, carbon black etc., on the tubes. Specifically, carbon black would in any case be avoided because of the possibility of future corrosion of stainless steel tubes under operating conditions.

Method of Formation

(a) Single Layer Hydrous Zirconium (iv) oxide Membranes. A solution containing either 2 000 or 5 000 mg/ℓ $NaNO_3$ and 10 mg/ℓ Zr(iv) was prepared and adjusted to a pH below 4 but above 3 with nitric acid (usually pH 3.5). This solution was circulated (by-passing the support tube) until thoroughly mixed and the desired temperature had been reached. A temperature of 40°C was maintained in the tests unless otherwise specified.

When temperature and pH were correct, the porous support was put into circuit and pressurisation and circulation through the support begun; the permeability decreased and pressure increased. The permeability and pressure versus time was measured during this stage. The rejection (based on conductivity) was monitored and the presence of zirconium in the permeate determined. Levels could be set to suit objectives.

(b) Composite Membrane - Using a Chelating Compound such as Polyacrylic Acid. Excess zirconium was rinsed from the loop circuit and tank with clean reverse osmosis permeate water, adjusted to pH 4 with nitric acid.

A solution containing 50 mg/ℓ polyelectrolyte and either 2 000 mg/ℓ or 5 000 mg/ℓ $NaNO_3$ was prepared and adjusted to about pH 2 and the temperature increased to the desired level. A temperature of 40°C was maintained in the tests unless otherwise specified.

When temperature and pH were correct, the solution was circulated through the porous support for 30 minutes. After this time, the pH was raised to about 3 and maintained at this pH for another 30 minutes. After each 30 minutes, the pH was raised by one unit until the solution was near neutral. During this process, the rejection of sodium nitrate by the membrane increased and the flux decreased. The excess PAA was rinsed from the system with reverse osmosis permeate. The supports were then stored wet for further tests.

The method was based on that used by Johnson, *et. al.* (ref. 2). The conditions specified in (a) and (b) above were maintained unless otherwise specified.

RESULTS

It was found that in preparing the hydrous zirconium (iv) oxide membranes, the zirconium deposited easily on the porous tubes in spite of the relatively large pore size. This was achieved either by closing the by-pass valve slowly, until the desired inlet pressure was achieved, or by closing the by-pass valve immediately on passing feed through the tube to give the desired inlet pressure. Velocity was maintained by altering pump motor speed.

Typical flux decline patterns at low inlet pressures (300 kPa) are given in Figs. 2 and 3 for membrane formation on different tubes and on a single tube (T4) respectively . Thus even with tests repeated using the same tube there was some difference. The initial permeability may have some effect but more tests are necessary to determine the critical factors.

The ionic rejection for the second series is given in Table 1. Even at very low concentrations of zirconium in the feed, a membrane could be formed.

Using tube T4 again, two tests were carried out on the formation of composite zirconium/PAA membranes at 300 kPa inlet pressure and a cross-flow velocity of 1.25 m/s. The results are depicted in Fig. 4.

The zirconium feed was a solution of 5 mg/ℓ Zr and 2 000 mg/ℓ $NaNO_3$ at pH 3.5. After formation of the hydrous zirconium (iv) oxide membrane, the tube was then membraned with a solution containing 50 mg/ℓ polyacrylic acid. The pH was varied from 2.2 by approximately one pH unit every 30 minutes to pH 7. The composite membrane was then stripped off and the tube remembraned under similar conditions. Clearly membranes are readily formed even at these low pressures and the composite membrane tended to settle down to the same flux level.

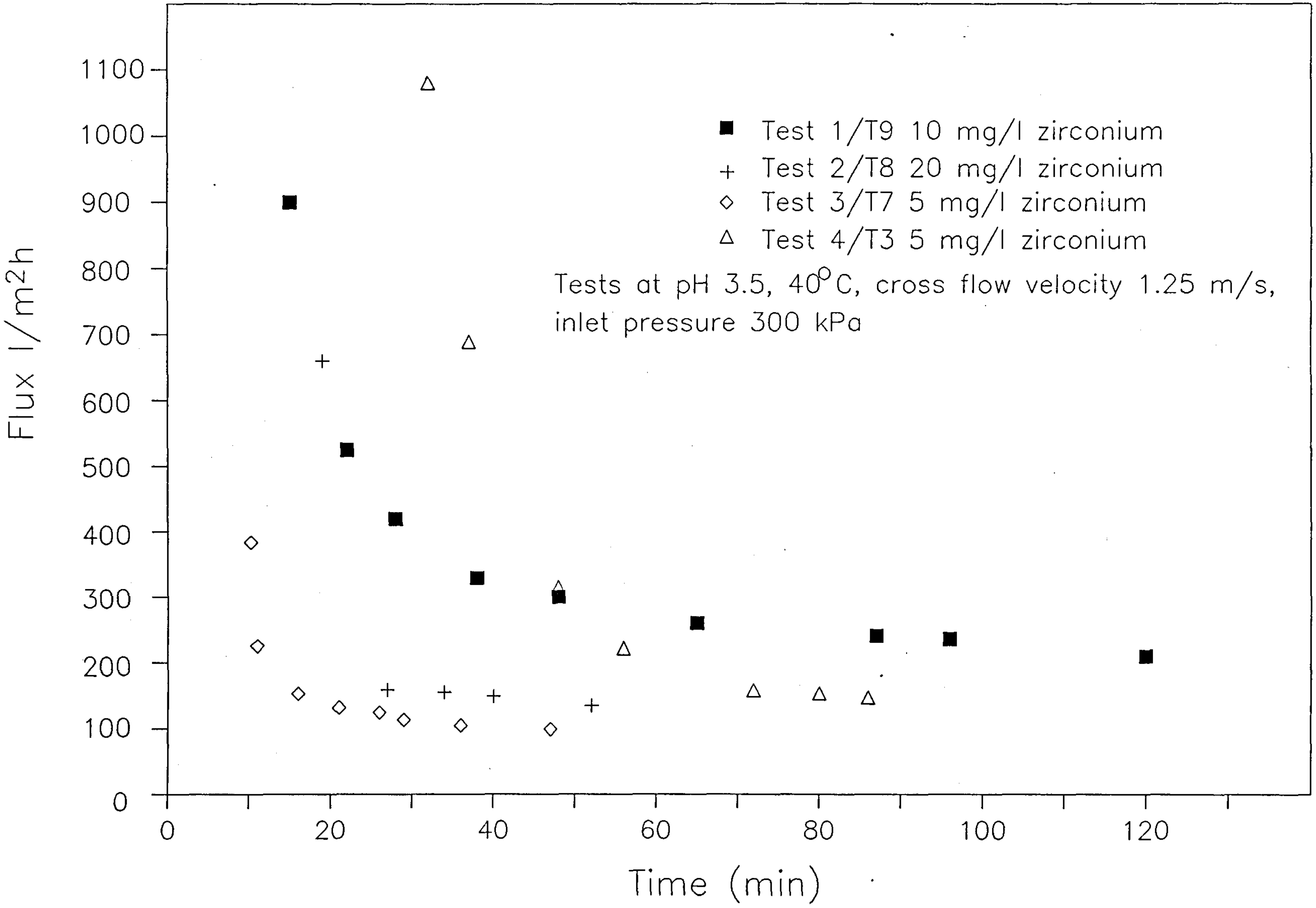


Fig. 2. Typical Patterns of Flux Decline with Time of Formation of Zirconium Membrane (different tubes)

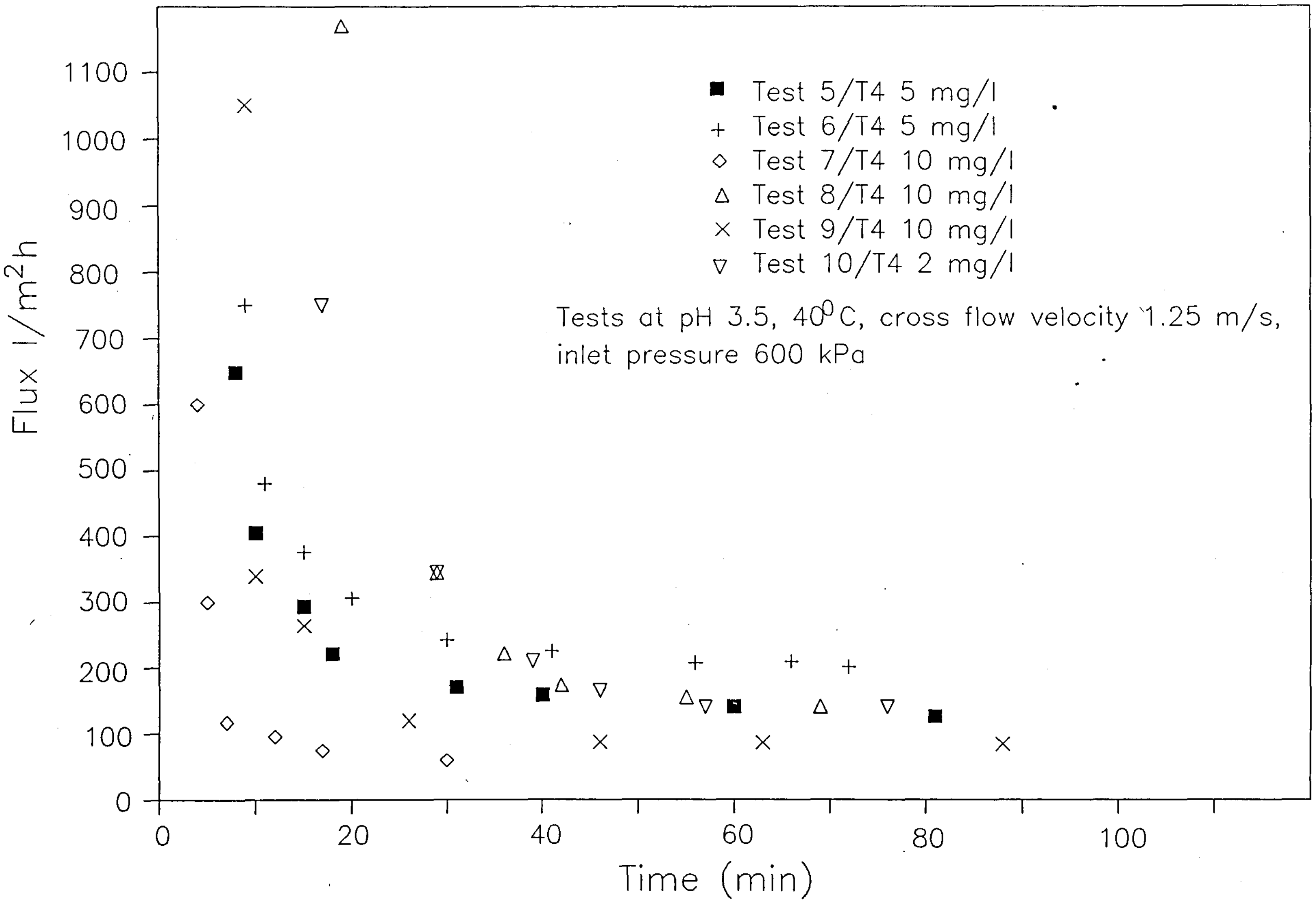


Fig. 3. Typical Patterns of Flux Decline with Time of Formation of Zirconium Membrane (single tube)

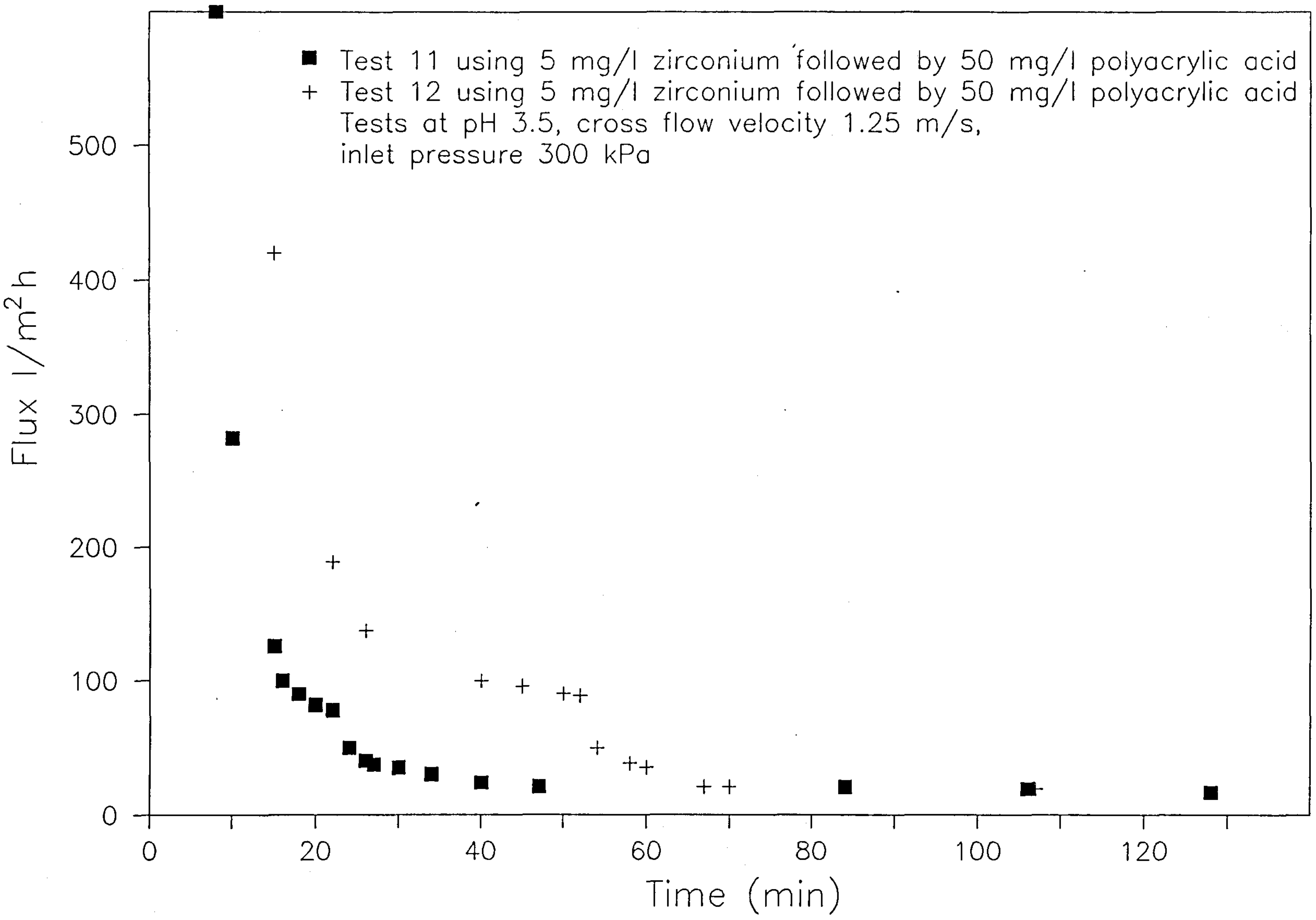


Fig. 4. Formation of Hydrous Zirconium (iv) Membrane Followed by Zirconium/Polyacrylic Acid Membrane

TABLE 1
Ionic rejection for membranes formed with different concentrations of zirconium in feed

Tests	Rejection* %	Flux ℓ/m^2h	Approx. Zr in feed mg/ℓ	Cross-flow velocity m/s
5 T4	10.6	170	5	1.25
6 T4	10.4	205	5	1.25
7 T4	13.7	75	10	1.25
8 T4	18.0	87	10	1.25
9 T4	13.1	141	10	1.25
10 T4	5.3	139	2	1.25

* Rejection based on conductivity of solution to which 2 000 mg/ℓ $NaNO_3$ had been added (pH 3.5). Rejection is the apparent salt rejection given by the relation Robs = 1 - C_p / C_f where C_p and C_f are the product and feed concentrations or conductivities respectively.

The next series of tests was carried out at formation pressures varying from just above atmospheric to 600 kPa on porous stainless steel tubes. The results of these are summarised in Table 2.

TABLE 2
Flux and rejection for various conditions of formation of composite membranes (Zr-PAA)

Test	13 T4	14 T9	15 T5	16 T2	17 T7	18 T3	19 T3	20 T8	21 T6	22 T1
Pressure of formation (kPa)	600	600	600	600	600	600	300	200	100	atmos
Velocity during formation (m/s)	1.25	1.25	1.25	1.25	1.25	0.25	0.1	0.25	0.25	0.1
Zr layer deposited at pH	3.5	3.88	3.04	3.9	2.6	3.54	3.55	3.55	3.55	3.51
Zr concentration in feed (mg/ℓ)	10	10	10	10	10	10	10	10	10	10
Flux (ℓ/m^2h) at kPa:										
600 *1	28	31	14	14	17	33	55	63	30	-
3 600 *2	90	132	63	63	93	111	196	180	225	2 910
6 000 *3	165	183	126	120	216	210	312	270	636	4 865
Robs % *4 on 2 000 mg/ℓ $NaNO_3$										
at kPa 600	31	39	39	36	28	32	33	33	37	-
3 600	66	66	57	66	48	69	64	54	55	0
6 000	69	73	54	70	41	73	69	58	27?	0
Retest at low pressure after storage in water for three months pressure of test: 600 kPa; cross-flow velocity 1.2 m/s; pH near 6.5										
Flux ℓ/m^2h	29	39	25	-	-	-	-	47	50	-
Robs %	28	36	32	-	-	-	-	29	27	-

*1 Velocity through tube approx. 1.3 m/s.
*2 Velocity through tube approx. 5.0 m/s.
*3 Velocity through tube approx. 5.0 m/s.
*4 Dual layer tests at pH 6 to 7.

Rejection and flux properties were tested using sodium nitrate solutions of 2 000 mg/ℓ concentration and at pressures varying from formation conditions to 6 000 kPa.

Values for rejection for membranes formed between 300 and 600 kPa are satisfactory even when the cross-flow velocity of the membraning solution during formation was as low as 0.1 m/s. The tests in which the zirconium had been deposited at pH 2.6 and 3.0 gave lower than normal rejection values at the higher pressure of 3 600 to 6 000 kPa. There was a distinct dropping off of the rejection values at high test pressures for membranes formed at pressures below 300 kPa; flux increase with pressure indicated failure of membranes formed at pressures below 200 kPa.

Rejection and flux tests at low pressure (600 kPa) done after high pressure testing and storage in water for three months, indicated that the membranes were stable. Allowing for the difference in permeability in the naked tubes, the above results do demonstrate that satisfactory membranes can be formed at low pressures (above 300 kPa) and low liquid flow velocities (0.1 m/s). pH is undoubtedly an important parameter and hydrous zirconium (iv) oxide should be deposited above pH 3.

Membraning of large porous stainless steel modules (Carre Inc.) was carried out at high pressure (6 000 kPa inlet) at the same time as the low pressure formation tests were in progress. The large modules consisted of three tube bundles and, for the purpose of membraning the tube bundles, they were treated independently. The total area of a complete module (porous section) was 6.35 m^2 with a total support length of 134.5 m. The porous section was of the same nature as that used in the low pressure tests described.

A typical result for the zirconium membrane prepared at 6 000 kPa and a cross-flow velocity at tube exit of 5.3 m/s was

Flux = 400 ℓ/m^2h.

Rejection* = 50% (2 000 mg/ℓ $NaNO_3$ at pH 3.3 to 3.4).

After wet storage (1 month), the module was retested and results were:

Flux = 550 ℓ/m^2h.

Rejection* = 30%.

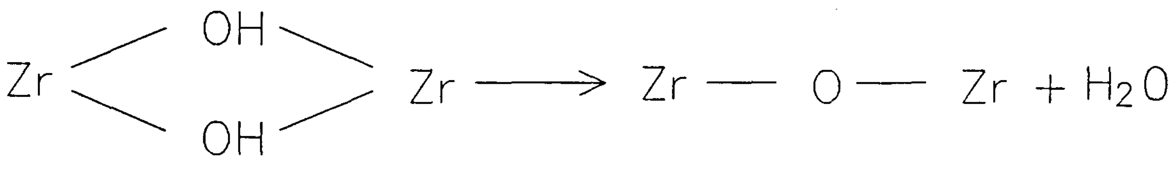
* Rejection on long tubes is given as:

$R_{obs} = 1 - C_p/C_f$

where C_f = $^1/_2$ (feed + rejection concentration or conductivity).

C_p = permeate concentration or conductivity.

It is believed that the reason for the loss of membrane performance in rejection is that the hydrous zirconium oxide membrane, which has bridged hydroxyl groups, undergoes the oxolation reaction during storage:



This reaction will not, however, affect subsequent reaction with polyelectrolytes like polyacrylic acid.

A series of tests was also conducted on smaller "hair-pin" bend porous stainless steel tubes, with 0.142 m^2 porous section, using the high pressure membraning technique (6 000 kPa and cross-flow velocity at tube exit = 4.2 m/s). In these tests typical results were:

Flux = 310 ℓ/m^2h.

Rejection = 35% (5 000 mg/ℓ $NaNO_3$ and pH 3.6).

Hydrous zirconium oxide membranes were thus readily formed even on very long tubes and these tubes were then treated with polyacrylic acid solution under standard conditions (6 000 kPa pressure). A typical result is given below (cross-flow velocity at tube exit = 5 m/s).

	Zirconium membrane	Zr-PAA membrane
Flux ℓ/m^{2}h	380	80
Rejection % (conductivity)	36*1	70.7*1 73*2
pH	3.5	6.3

*1 Rejection from a solution containing 5 000 mg/ℓ $NaNO_3$.

*2 Rejection from a solution containing 2 000 mg/ℓ $NaNO_3$.

It will be noted from Table 2 that composite layer tests at low pressure tend to show somewhat lower ionic rejection than those at high pressure. The flux, however, is higher.

In an attempt to obtain further information on the relation between primary zirconium membranes and final Zr/PAA membranes, a series of tests was conducted as follows: the primary zirconium membrane was laid down from a solution containing 10 mg/ℓ Zr, at pH 3.5 at different cross-flow velocities and at an inlet pressure of 600 kPa. The Zr/PAA membrane was prepared at 600 kPa and a fixed cross-flow velocity of 1.25 m/s. The results are summarised in Figs. 5 and 6 and Table 3.

There is a large scatter in rejection capability as may be seen from Fig. 6. The low rejecting hydrous zirconium (iv) oxide membranes were often those produced at low velocity. Such membranes did not, however, produce particularly low quality composite membranes; see test 31 in Table 3.

Again, in these tests, the composite membranes formed at low pressure and low cross-flow velocity (1.25 m/s) were capable of showing reasonable rejection and good fluxes when evaluated at high pressure.

Membrane Formation on Stainless Steel Tubes with Modified Pore Size

The large variation in flux and rejection for the membranes prepared on the stainless steel supports is probably due to the large pore size and the variation in pore size. Various materials were considered for deposition in the pores for size modification. It was decided to use fumed silica. The product selected was Cab-O-Sil, M·5 produced by Cabot Corp. The material is produced by the hydrolysis of vaporized silicontetrachloride in a flame of hydrogen and oxygen. The physical properties of the material are:

Surface area m^2/g	200 - 400
Nominal particle size (diam. in microns)	0.007 - 0.014
325 mesh residue	0.02%
X-ray form	amorphous
SiO_2	>99.8%.

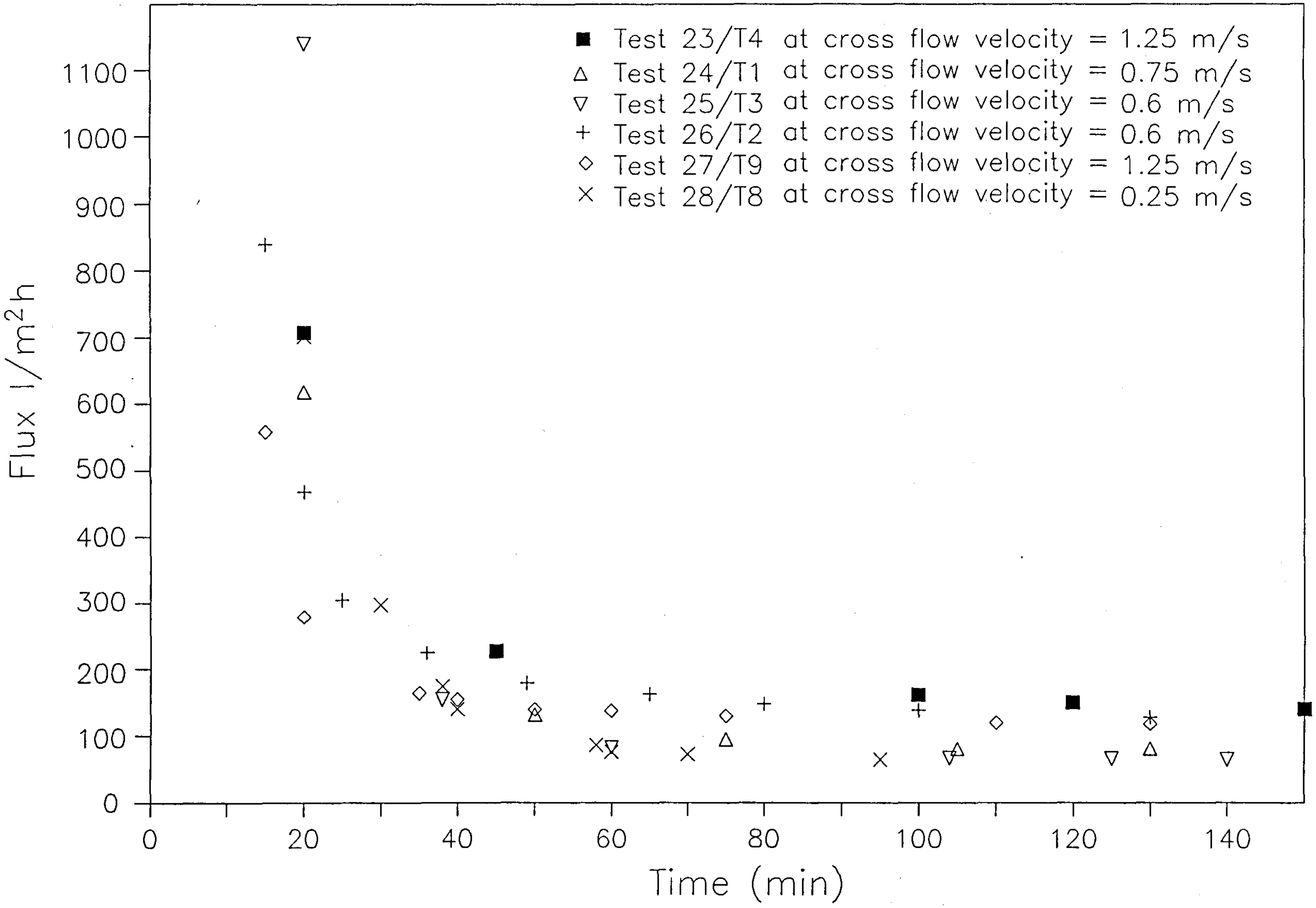


Fig. 5. Flux Decline During Formation of Hydrous Zirconium (iv) Oxide Membranes

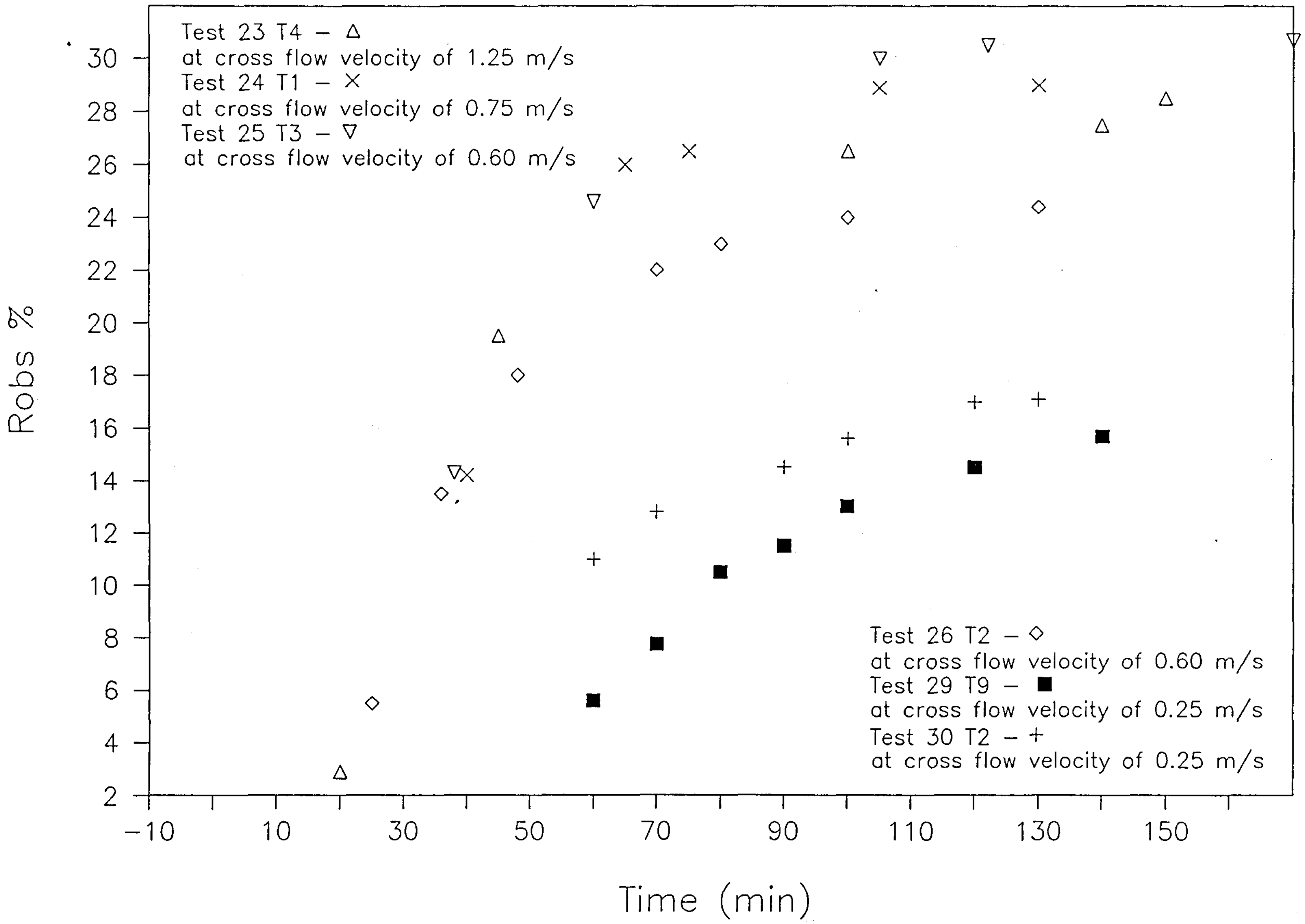


Fig. 6. R(obs) During Formation of Hydrous Zirconium (iv) Oxide Membranes

TABLE 3

Flux and rejection for membranes prepared at low pressure (600 kPa)

Test	31	32	33	34
Cross-flow velocity during Zr membrane formation	0.25	1.25	0.60	1.25
Flux ℓ/m^{2}h Zr membrane at 600 kPa after 120 min	60	120	130	150
Robs % after 120 min at pH 3.5	20	29	24	28
Flux ℓ/m^{2}h Composite Zr/PAA membrane at				
600 kPa	29	32	49	52
cfv*	1.25	1.25	1.25	1.25
3 600 kPa	96	87	183	114
cfv	4.2	4.2	4.7	4.7
6 000 kPa	163	180	300	300
cfv	3.8	3.8	4.2	4.0
Robs % at				
600 kPa	36	38	35	35
3 600 kPa	58	67	62	60
6 000 kPa	60	67	64	61
pH 6.7 - 7 2 000 mg/ℓ $NaNO_3$ solution				

*cfv = cross-flow velocity, m/s, during evaluation.

A required quantity of the silica was carefully creamed before mixing into the bulk of the water in the feed tank. Tubes were treated by passing the aqueous suspension of 10 to 20 mg/ℓ of the fumed silica tangentially across the inner surface of the porous tube. The inlet pressure was 600 kPa and the cross-flow velocity was 1.25 m/s. Flow was maintained for about 60 minutes, during which time the flux had settled down to a steady level. Thereafter the tubes were stored in water, pending deposition of a hydrous zirconium (iv) oxide membrane. The deposit of silica was stable and was not removed by fluid flow through the tubes even after storage in water. The pore size of the tubes had been considerably modified as may be seen from the values given in Table 4. The spread had also been reduced.

TABLE 4

Pore size of porous stainless steel tubes before and after treatment with fumed silica

		Maximum pore size micron	Mean pore size micron
Tube T8	before	5.6	2.7
	after	3.4	2.2
Tube T7	before	4.3	2.2
	after	2.4	1.7

The tubes treated with fumed silica were then subjected to the standard procedure for deposition of zirconium at 600 kPa inlet pressure and cross-flow velocity of 1.25 m/s. It was found that the tubes coated readily and tended to settle down to a flux somewhat higher than that achieved with tubes which had not been pretreated with silica. The ionic rejection from a 2 000 mg/ℓ solution of sodium nitrate was marginally lower than that obtained with untreated tubes. Some results are summarised in Figs. 7A and 7B.

On treatment with polyacrylic acid in the usual manner at 600 kPa and cross-flow velocity of 1.25 m/s, to form a composite membrane, it was found that the flux settled down at about 60 ℓ/m^2h, somewhat higher than for untreated tubes with composite membranes (Table 3). The comparison between flux and rejection for hydrous zirconium (iv) oxide and Zr/PAA membranes formed on tubes pretreated with silica, is given in Table 5.

TABLE 5

Comparison of flux and rejection Zr and Zr/PAA membranes formed on pretreated porous stainless steel tubes

Tube No.	Zr Membrane		Zr/PAA Membrane	
	Flux ℓ/m^2h at 600 kPa	Rejection*1 %	Flux ℓ/m^2h at 600 kPa	Rejection*2 %
T1	195	27	61	33
T3	200	27	65	34
T7	238	27	69	27
T8	240	26	60	30
T2	220	27	58	33
T7	230	27	58	27
T9	198	27	-	-

*1 from a solution containing 2 000 mg/ℓ $NaNO_3$ at pH 3.5; cross-flow velocity 1.25 m/s.

*2 from a solution containing 2 000 mg/ℓ $NaNO_3$ at pH 6.8 - 7; cross-flow velocity 1.25 m/s.

High Pressure Operation/Evaluation

Some of the composite membranes formed at 600 kPa on pretreated porous stainless steel tubes were tested for flux and rejection at higher pressures (3 000 and 6 000 kPa), using sodium nitrate solutions containing 2 000 mg/ℓ $NaNO_3$ at pH 6.9 to 7.2. The results are given in Table 6.

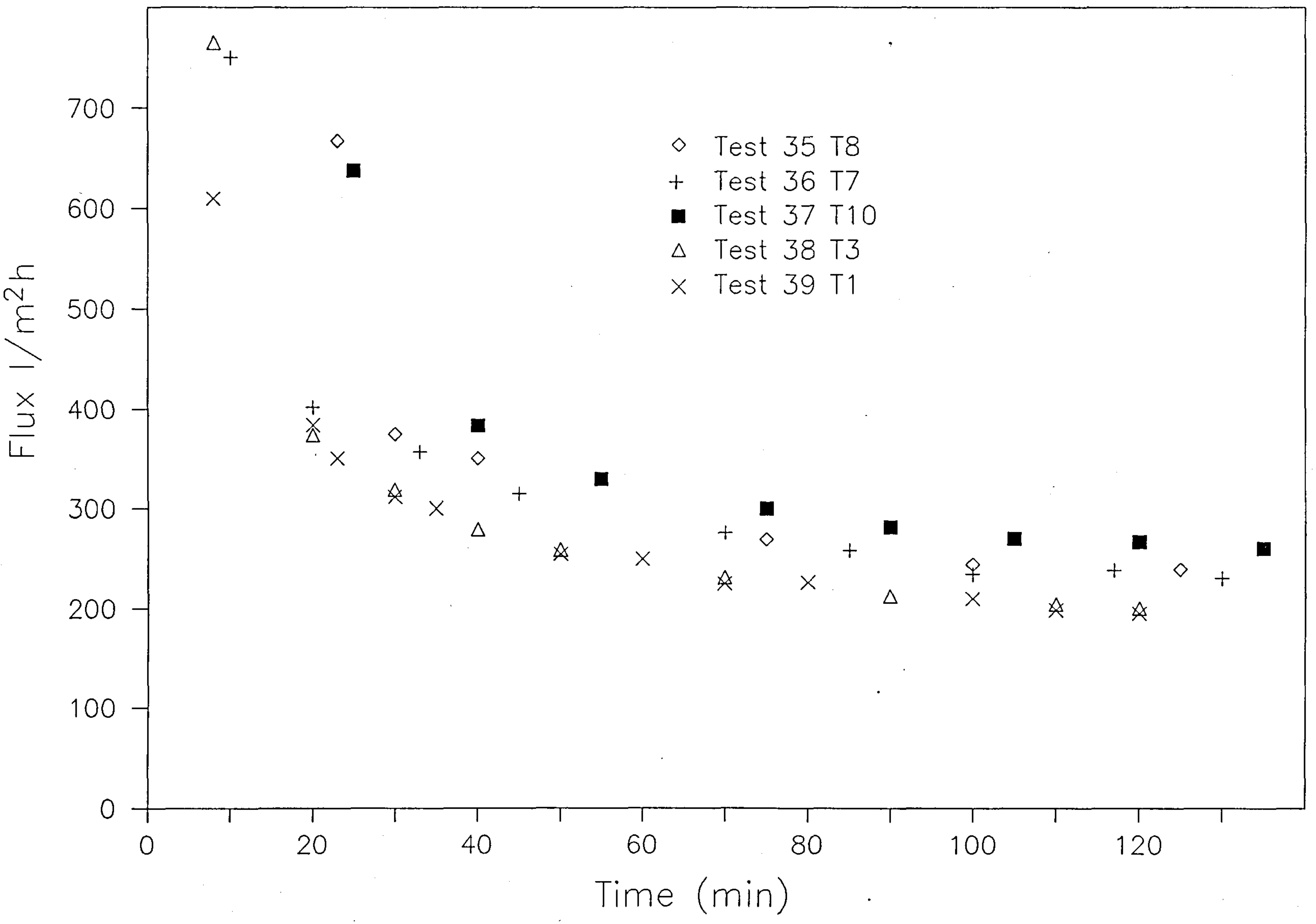


Fig. 7A. Hydrous Zirconium (iv) Oxide Membrane Prepared on Porous Stainless Steel Tubes Pretreated with Fumed Silica

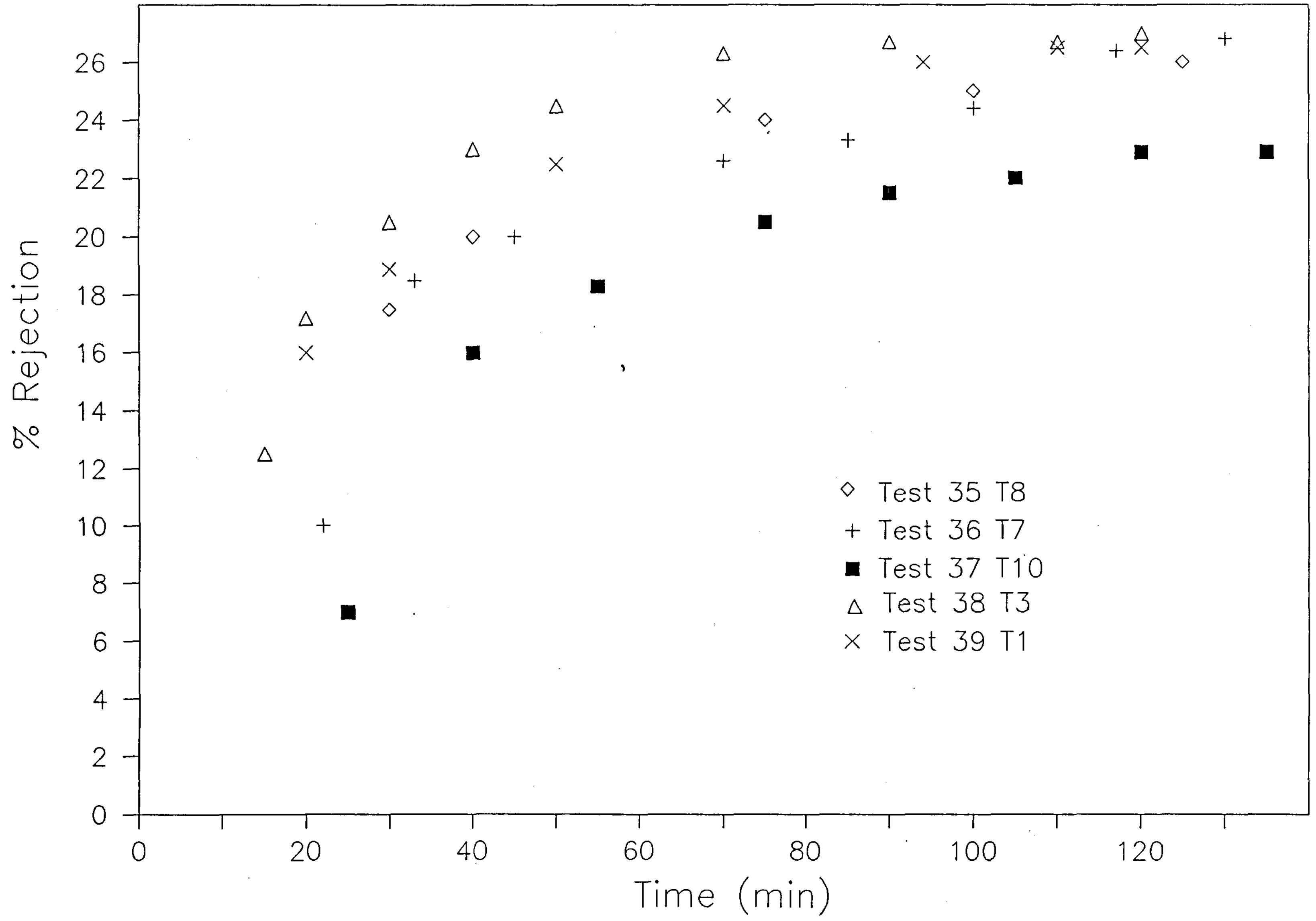


Fig. 7B. Hydrous Zirconium (iv) Oxide Membrane Prepared on Porous Stainless Steel Tubes Precoated with Fumed Silica

It will be seen that the composite membranes operated at higher flux than the composite membranes prepared on tubes that had not been pretreated (Table 2). Rejection at the higher pressures (3 000 to 6 000 kPa) was, however, lower than that obtained on membranes formed on naked tubes.

TABLE 6

Flux and rejection for composite membranes formed on pretreated stainless steel tubes at 600 kPa and at a cross-flow velocity of 1.25 m/s

Tube No.	Flux ℓ/m^{2}h at			Rejection % at					
	600 kPa	3 000 kPa	6 000 kPa	600 kPa	cfv*	3 000 kPa	cfv*	6 000 kPa	cfv*
T1	61	198 (23°C)	360 (26°C)	33	1.25	43	2.8	40	2.8
T3	65	258 (35°C)	245 (28°C)	34	1.25	46	2.8	45	2.8
T2	58	222 (30°C)	495 (33°C)	33	1.25	41	2.8	31	2.8
T5	58	330 (40°C)	660 (40°C)	27	1.25	30	2.8	23	2.8

* cfv = cross-flow velocity, m/s.

These high pressure evaluation tests were carried out at cross-flow velocities which were too low to overcome the polarisation at the membrane surface caused by the high permeate fluxes.

Further tests were thus conducted to show the effectiveness of pretreatment.

The Pretreatment Procedure Using Suspensions of 2 mg/ℓ Silica

A 2 gram sample of Cab-O-Sil was creamed and then diluted to about 200 mℓ and subjected to agitation with a high frequency vibratory agitator (Chemap). The well dispersed concentrate was further diluted to 1 000 mℓ and again agitated.

A suitable aliquot portion of the stable suspension was then dispersed in 50 ℓ of solution used in the low pressure cross-flow rig or in 100 ℓ used in a high pressure rig. The pH was adjusted to about 3.5 and the silica content was 2 mg/ℓ.

The solution was passed through the naked porous stainless steel tubes at a selected cross-flow velocity at a selected inlet pressure. Flow was continued until the flux had settled down to a "steady" value, usually after one hour.

Tests at Formation Pressures of 600 kPa

Two tubes were coated with silica (2 mg/ℓ) at a cross-flow velocity of 1.25 m/s and at an inlet pressure of 600 kPa. A zirconium membrane was then deposited in the usual manner. The zirconium membrane was subsequently chelated with polyacrylic acid in the usual manner.

The results are given in Table 7.

These results are similar to those achieved with tubes which had been treated with silica suspensions of high concentration (Table 5).

The two tubes were also tested at different pressures and cross-flow velocities. Results are shown in Table 8 for Tube T3 which gave similar results to Tube T5.

Cross-flow velocity has a marked effect on rejection at the high pressure, high flux conditions.

These tests were followed by others at higher cross-flow velocities. The results are given in Table 9.

TABLE 7

Characteristics of membranes formed on pretreated tubes

Test	Tube	Membrane	Cross-flow velocity m/s	Flux at 600 kPa after 120 min ℓ/m^2h	Rejection Robs % at pH 3.5; (2 000 mg/ℓ $NaNO_3$ soln)
35	T5	Zr	1.25	201	29
36	T3	Zr	1.25	252	24
				Flux at 600 kPa after 1 hr ℓ/m^2h	Rejection Robs % at pH 6-7; (2 000 mg/ℓ $NaNO_3$ soln)
35/1	T5	Zr/PAA	1.25	56	34
36/1	T3	Zr/PAA	1.25	62	34

TABLE 8

Composite membrane (Tube T3) tests at different pressures and cross-flow velocities

Press kPa	Flux ℓ/m^2h	Cross-flow velocity m/s	Rejection % at pH 6 - 7 (2 000 mg/ℓ $NaNO_3$)
600	55	2.4	27
1 000	85	2.3	40
2 000	175	2.0	49
3 000	260	1.8	47
4 000	360	1.75	42
6 000	530	1.55	34
6 000	530	0.7	18
6 000	530	0.25	6.5

TABLE 9

Characteristics of composite membrane at high pressure and high cross-flow velocity

Test	Tube	Membrane	Cross-flow velocity m/s	Pressure kPa	Flux ℓ/m^2h	Rejection % at pH 6- 7 (2 000 mg/ℓ $NaNO_3$)
36/2	T3	Zr/PAA	4.4	3 000	237	58
			4.3	6 000	504	59
35/2	T5	Zr/PAA	4.9	3 000	216	56
			4.3	6 000	522	56

Clearly then, membranes formed at 600 kPa on pretreated tubes can be operated at higher pressures to give good rejections, provided that at high flux, high pressure conditions, a high cross-flow velocity is maintained to avoid polarisation.

Formation of Membranes at 2 000 kPa

A few tests were performed to determine whether formation at a somewhat higher pressure (2 000 kPa) improved the performance of the membrane. Composite membranes were prepared on tubes which had also been precoated at 2 000 kPa with Cab-O-Sil.

The results are given in Table 10 together with results for a membrane on a naked tube.

TABLE 10

Tests on composite membranes prepared on treated and untreated tubes

Test pressure kPa		Composite membrane formed at 600 kPa on pretreated tube				Composite membrane formed at 2 000 kPa on pretreated tube		Composite membrane formed at 2 000 kPa on naked tube	
		Test No.				Test No.		Test No.	
		36/1	cfv*1	25/1	cfv*1	37/1	cfv*1	38/1	cfv*1
600	Flux ℓ/m^2h	62	1.25	56	1.25				
	Rejection %	34		34					
2 000	Flux ℓ/m^2h					168	3.8	30	3.9
	Rejection %					58		59	
3 000	Flux ℓ/m^2h	237	4.4	216	4.9	252	4.6	57	4.5
	Rejection %	58		56		67		60	
6 000	Flux ℓ/m^2h	540	4.3	522	4.3	588	4.2	111*2	3.9
	Rejection %	59		56		67		55	

Rejection at pH 6 - 7; 2 000 mg/ℓ $NaNO_3$ solution.

*1 cfv = cross-flow velocity, m/s.

*2 Membrane gave very high flux on changing to higher pressure but declined slowly to a steady value. This high increase above "steady" value did not occur with membranes on pretreated tubes.

These tests indicate that the membrane formed at the higher pressure (2 000 kPa) on a pretreated tube is somewhat superior to the membrane formed at 600 kPa on pretreated tubes. The membrane formed at 2 000 kPa on a naked tube gave a disappointing flux.

The speed of hydrous zirconium oxide membrane formation for pretreated and naked porous stainless steel tube is shown in Figures 8 and 9. It will be seen that there is a more rapid decline of flux on the pretreated tube. Rejection properties become apparent after a shorter time as well. However, both tubes show similar rejection values when the flux values settle down. The respective fluxes are, however, significantly different.

Figure 10 shows the decline of flux with time for two conditions used in these tests for precoating the stainless steel tubes. Low pressure deposition was done at 600 kPa and at a cross-flow velocity of 1.25 m/s whereas the higher pressure deposition was done at 2 000 kPa and at a cross-flow velocity of 3.6 m/s.

Formation of Membranes when Precoating Material is Used Together with Hydrous Zirconium (iv) Oxide

A few tests were carried out with a mixture of Cab-O-Sil (2 mg/ℓ) and hydrous zirconium (iv) oxide (10 mg/ℓ) in the feed vessel of the rig. The zirconium membranes and subsequently the Zr/PAA membranes were formed under standard conditons at 600 kPa and at a cross-flow velocity of 1.25 m/s. The results are given in Table 11.

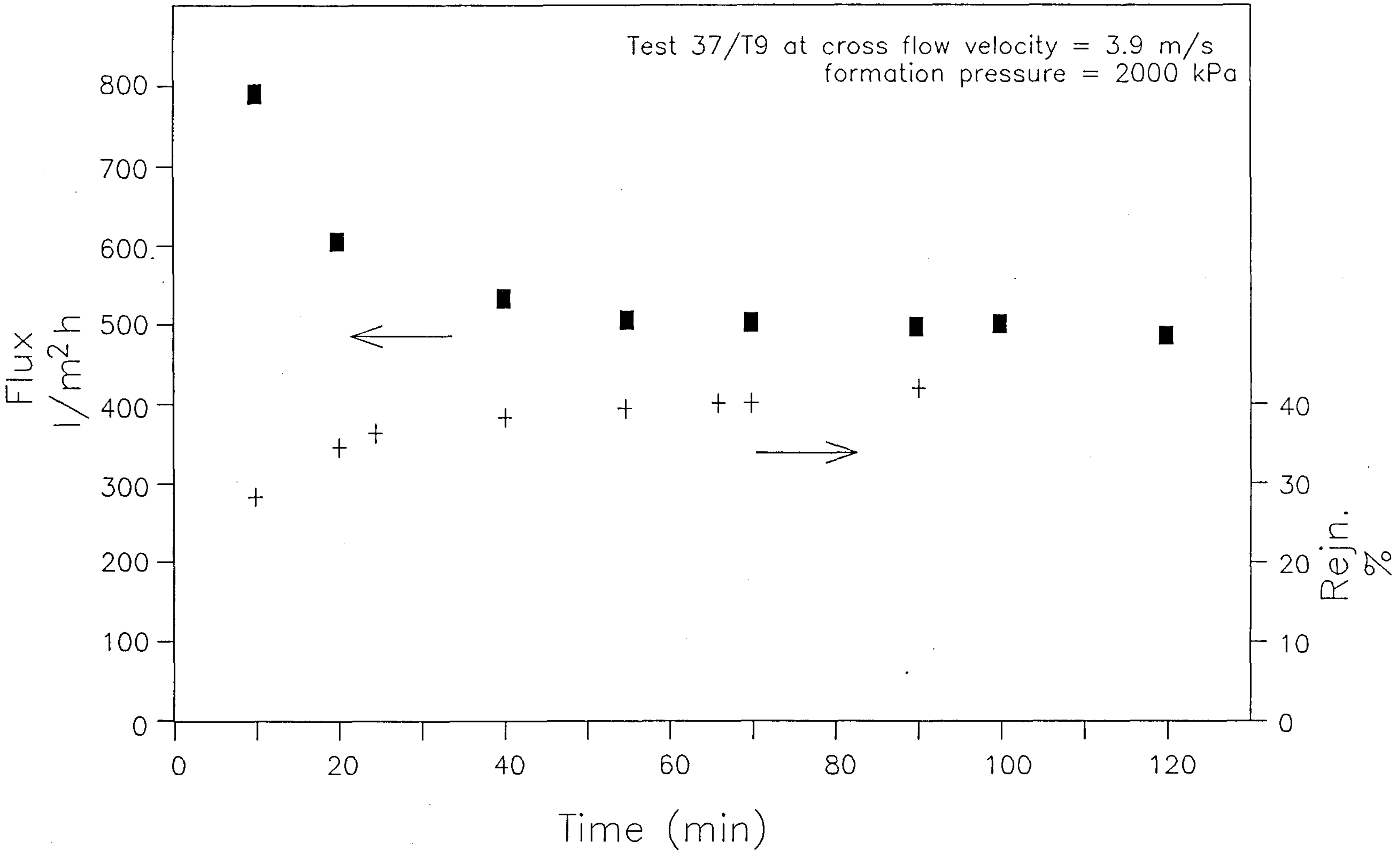


Fig. 8. Zr Membrane on Pretreated Tube

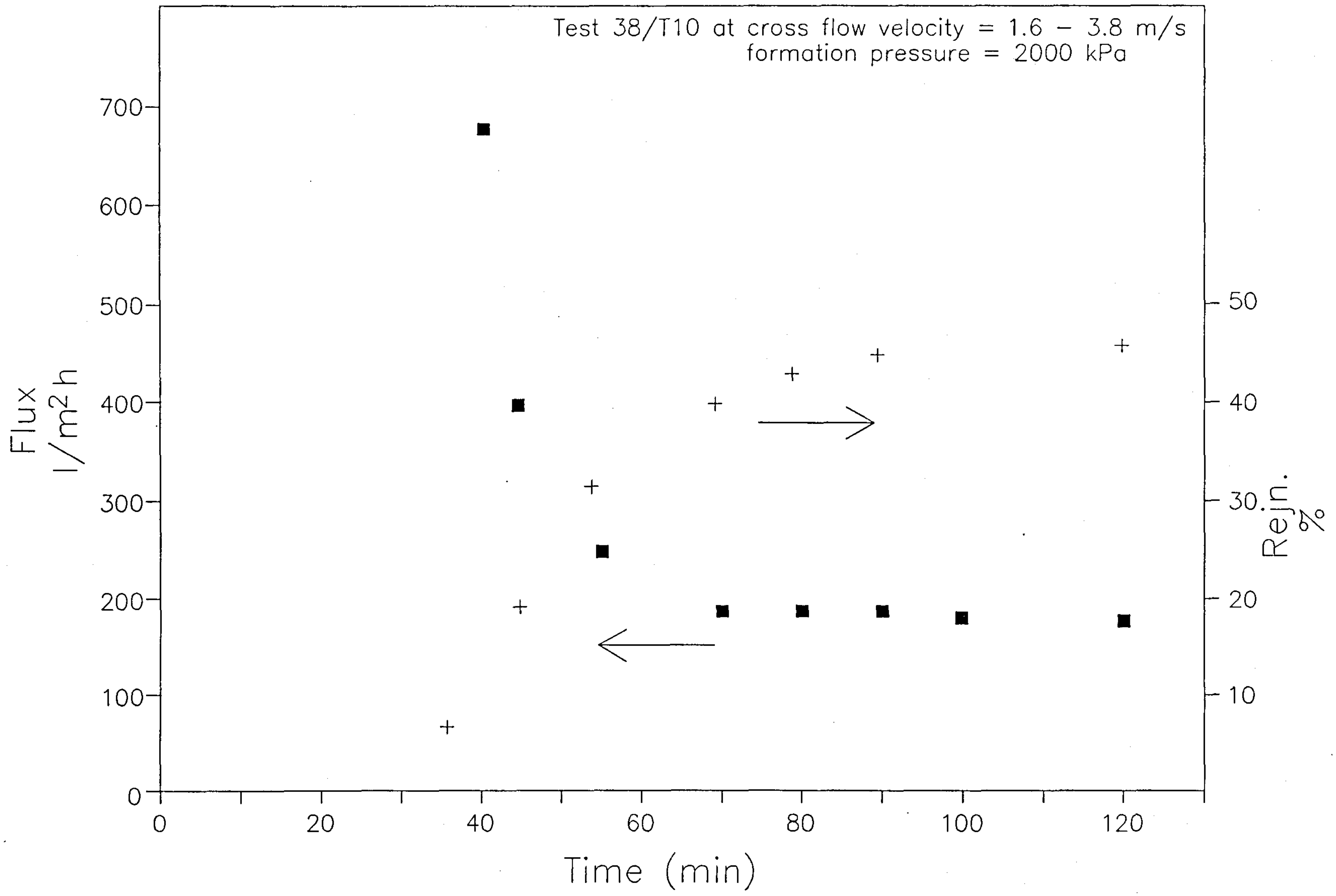


Fig. 9. Zr Membrane on Naked Tube

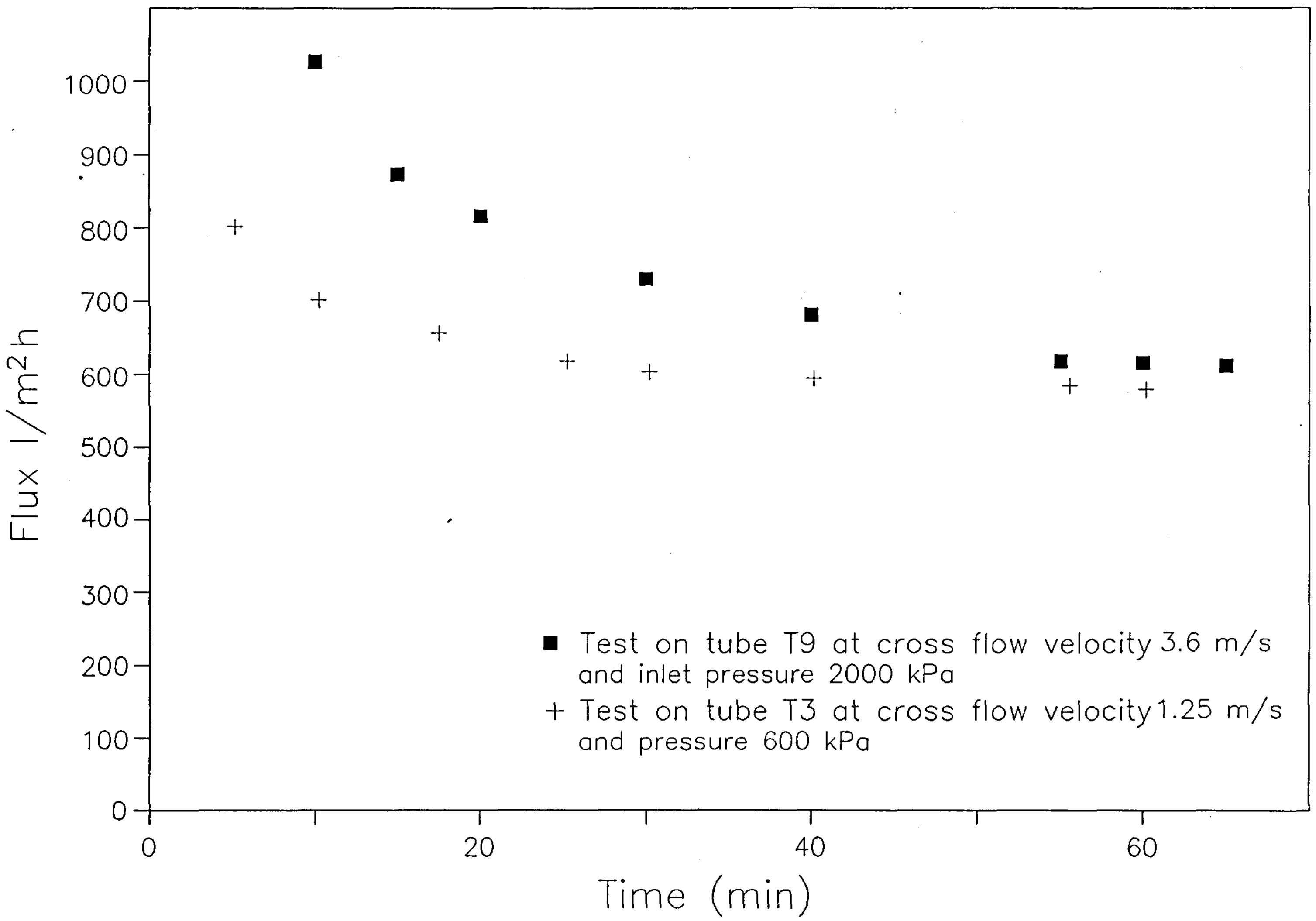


Fig. 10. Treatment of Porous Stainless Steel with Cab–O–Sil (2 mg/l)

TABLE 11

Characteristics of zirconium and Zr/PAA membranes: Silica added to the hydrous zirconium oxide feed for formation of zirconium membrane

Test No.	pH	Membrane	Pressure kPa	Cross-flow velocity m/s	Flux ℓ/m²h	Rejection* (2 000 mg/ℓ $NaNO_3$)
39	3.5	Zr	600	1.25	142	29
39/1	6-7	Zr/PAA	600	1.25	21	58
		Zr/PAA	3 000	4.9	114	68
		Zr/PAA	6 000	4.3	195	74
40	3.5	Zr	600	1.25	104	33
40/1	6-7	Zr/PAA	600	1.25	13	32
		Zr/PAA	3 000	4.8	75	65
		Zr/PAA	6 000	4.2	150	69

* Rejection at pH 3.5 for zirconium membrane; at pH 6-7 for composite membrane.

The membranes formed are no better than those formed in the absence of silica (see Table 2). Hence to form high flux membranes it is necessary to precoat the porous stainless steel tubes with a material such as Cab-O-Sil.

CONCLUSIONS

Composite membranes with variable but reasonable rejection and good flux were prepared at low pressure on naked porous stainless steel tubes (approximate values: flux 150 to 300 ℓ/m²h; rejection 60 to 70% at high cross-flow velocity at a pressure of 6 000 kPa).

When the pore size of the tubes was modified by "pore filling" with a fumed silica suspension, the degree of reproducibility of results in tests at 600 kPa improved markedly. The composite membranes prepared and tested at 600 kPa and 1.25 m/s cross-flow velocity on such pretreated tubes gave consistent flux values near 60 ℓ/m²h and rejection values near 30% for solutions containing 2 000 mg/ℓ $NaNO_3$.

When operated at higher pressures (6 000 kPa), the high permeate flux results in polarisation and cross-flow velocities need to be increased. At 6 000 kPa and a cross-flow velocity of 4.3 m/s, flux values over 500 ℓ/m²h and rejection values of about 60% can be achieved.

At formation pressures of 2 000 kPa slightly better membranes are formed with flux values approaching 600 ℓ/m²h and rejection values above 60%.

When the fumed silica is added to the hydrous zirconium (iv) oxide suspension during zirconium membrane formation, the zirconium membrane and the subsequently formed zirconium/PAA membrane behave as membranes on naked tubes. The results have demonstrated the remarkable ability of the colloidally dispersed hydrous zirconium (iv) oxide to "pore fill" and bridge the large pores sizes present in the naked stainless steel tubes used in these tests.

Some prior "pore filling" with a larger sized colloidally dispersed silica at very low concentrations improved the reproducibility of results and assisted in producing a high flux membrane which can be formed at low pressure and subsequently used at high pressure.

Further work in this field is necessary to examine the optimum formation pressure.

ACKNOWLEDGEMENTS

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APPENDIX 3

COMPARISON OF MEMBRANES PREPARED AT DIFFERENT PRESSURES ON POROUS STAINLESS STEEL TUBES :

NAKED AND PRETREATED

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January 1989

A. Membrane on Tubes Pretreated with a Suspension of Silica (2 mg/ℓ). Low Pressure (600 kPa) Formation; High Pressure Evaluation.

Test	Membrane	Tube	Inlet pressure kPa	Cross-flow velocity m/s	Flux ℓ/m^{2}h	Rejection %	Conductivity of feed solutions mS/cm
1074	-	T3	600	1,25	5 800	(pretreatment with silica)	
1074	Zr	T3	600	1,25	252	24	2,51
1076	Zr/PAA	T3	600	1,25	62	34	2,42
1083	Zr/PAA	T3	3 000	4,40	237	58	2,40
1083	Zr/PAA	T3	6 000	4,30	504	59	2,40

B. Membrane on Tubes Pretreated with a Suspension of Silica (2 mg/ℓ). High Pressure (2 000 kPa) Formation; High Pressure Evaluation.

Test	Membrane	Tube	Inlet pressure kPa	Cross-flow velocity m/s	Flux ℓ/m^{2}h	Rejection %	Conductivity of feed solutions mS/cm
1085	-	T9	2 000	3,70	5 885	(pretreatment with silica)	
1086	Zr	T9	2 000	3,90	480	41	2,47
1088	Zr/PAA	T9	2 000	3,80	168	58	2,25
1088	Zr/PAA	T9	3 000	4,60	252	67	2,25
1088	Zr/PAA	T9	6 000	4,20	585	67	2,25

C. Membrane on Tubes Pretreated with a Suspension of Hydrous Zirconia (2 mg/ℓ). Low Pressure (600 kPa) Formation; High Pressure Evaluation.

Test	Membrane	Tube	Inlet pressure kPa	Cross-flow velocity m/s	Flux ℓ/m^{2}h	Rejection %	Conductivity of feed solutions mS/cm
2013	-	T4	600	1,25	2 640	(precoating)	
2014	Zr	T4	600	1,25	198	21	2,84
2015	Zr/PAA	T4	600	1,25	55	35	2,52
2016	Zr/PAA	T4	2 000	3,90	140	56	2,34
2016	Zr/PAA	T4	3 000	4,00	207	62	2,34
2016	Zr/PAA	T4	6 000	3,70	366	65	2,34

D. Membrane On Tubes Pretreated with a Suspension of Hydrous Zirconia (2 mg/ℓ). High Pressure (2 000 kPa) Formation; High Pressure Evaluation.

Test	Membrane	Tube	Inlet pressure kPa	Cross-flow velocity m/s	Flux ℓ/m^{2}h	Rejection %	Conductivity of feed solutions mS/cm
2017	-	T9	2 000	3,90	4 608	(precoating)	
2018	Zr	T9	2 000	3,90	440	21	2,75
2022	Zr/PAA	T9	2 000	3,90	98	57	2,24
2022	Zr/PAA	T9	3 000	4,10	153	66	2,24
2022	Zr/PAA	T9	6 000	3,90	294	67	2,24
2019	-	T5	2 000	3,90	3 360	(precoating)	
2020	Zr	T5	2 000	3,90	480	26	2,68
2021	Zr/PAA	T5	2 000	3,90	99	62	2,28
2021	Zr/PAA	T5	3 000	4,40	156	69	2,25
2021	ZR/PAA	T5	6 000	3,90	333	68	2,25

E. Membranes on Naked Tubes - No Pretreatment. Low Pressure Formation; High Pressure Evaluation.

Test	Membrane	Tube	Inlet pressure kPa	Cross-flow velocity m/s	Flux ℓ/m^{2}h	Rejection %	Conductivity of feed solutions mS/cm
1025	-	T9	600	1,25	>20 000	-	-
1025	Zr	T9	600	1,25	118	29	2,65
1031	Zr/PAA	T9	600	1,25	32	38	2,57
1031	Zr/PAA	T9	3 600	4,20	87	67	-
1031	Zr/PAA	T9	6 000	3,80	180	67	-

F. Membranes on Naked Tubes - No Pretreatment. Low Pressure Formation; High Pressure Evaluation.

Test	Membrane	Tube	Inlet pressure kPa	Cross-flow velocity m/s	Flux ℓ/m^{2}h	Rejection %	Conductivity of feed solutions mS/cm
1087	-	T10	2 000	3,80	<73 000	-	-
1087	Zr	T10	2 000	3,80	168	42	2,35
1089	Zr/PAA	T10	2 000	3,90	30	59	2,25
1089	Zr/PAA	T10	3 000	4,50	57	60	2,25
1089	Zr/PAA	T10	6 000*	3,90	110	55	2,25

Note: Rejection values from Zr membrane at pH near 3.5. Rejection values from Zr/PAA membrane at pH near 7.

* Flux increased to over 1 200 ℓ/m^{2}h on changing pressure, then decreased to 110 ℓ/m^{2}h over an hour; rejection, in turn, decreased to 6 % and gradually increased again. Pretreated tubes did not exhibit this phenomenon; flux and rejection values were reached rapidly after pressure changes. In this respect the silica treated tubes showed excellent stability.

G. Membrane on Naked Porous Stainless Steel Tube. High Pressure (6 000 kPa) Formation; High Pressure Evaluation

Test	Membrane	Tube	Inlet pressure kPa	Cross-flow velocity m/s	Flux ℓ/m^{2}h	Rejection %	Conductivity of feed solutions mS/cm
2023	-	T7	1 000	1,90	36 300	(naked tube)	
2023	Zr	T7	1 000 - 6 000 over 20 min then 6 000	-	high	-	-
2023	Zr	T7	6 000	1,60 - 3,90	67 000 to 420	over 130 min	
2023	Zr	T7	6 000	3,90	420	47	2,55
2024	Zr/PAA	T7	6 000	3,70	87	66	2,20

This result is no better than result obtained on membranes prepared at lower pressures.

H. Membrane on the Tube Pretreated with Fumed Silica (3 mg/ℓ). High Pressure (6 000 kPa) Formation; High Pressure Evaluation.

Test	Membrane	Tube	Inlet pressure kPa	Cross-flow velocity m/s	Flux ℓ/m^{2}h	Rejection %	Conductivity of feed solutions mS/cm
2025	-	T1	1 000 - 6 000	*1	97 800*2	-	-
2026	Zr	T1	6 000	0,90 - 3,90	640	45	2,45
2027	Zr/PAA	T1	6 000	3,90	230	72	2,34
2027	Zr/PAA	T1	3 000	4,00	90	69	2,34
2027	Zr/PAA	T1	2 000	3,90	51	60	2,35

*1 No reject after 3 000 kPa.

*2 Final permeate flux at 6 000 kPa.

These results are disappointing when compared with results obtained at formation pressures of 2 000 kPa on pretreated tubes. They are, however, significantly better than results obtained on naked tubes (Test series G) especially with respect to flux.

I. Membrane on Tube Pretreated with Silica (2 mg/ℓ) Ensuring a Flow Through Tube at All Times. Silica Treatment from 1 00 to 4 000 kPa; Zr and Zr/PAA Membranes Formed at 6 000 kPa (Feed volume 100 ℓ).

Test	Membrane	Tube	Inlet pressure kPa	Cross-flow velocity m/s	Flux ℓ/m^2h	Rejection %	Conductivity of feed solutions mS/cm
2029	-	T2	1 000 - 4 000	2,10-3,90-3,10	pretreating with silica (2 mg/ℓ)		
	-	T2	4 000	3,10	37 200	-	-
2034	Zr	T2	6 000	4,30	636	54	2,54
2035	Zr/PAA	T2	6 000	4,30	250	80	2,25
2035	Zr/PAA	T2	3 000	4,80	100	76	2,27
2036	Zr/PAA	T2	2 000	3,80	57	68	2,27
2030	-	T10	1 000	2,00	36 000	(naked tube)	
2030	-	T10	1 000 - 4 000	3,30-3,90-2,00	pretreating with silica (2 mg/ℓ)		
	-	T10	4 000	2,00	60 000	-	-
2033	Zr	T10	6 000	4,30	672	41	2,46
2036	Zr/PAA	T10	6 000	4,30	240	81	2,28
2036	Zr/PAA	T10	4 000	4,50	140	80	2,28
2036	Zr/PAA	T10	3 000	4,60	96	76	2,27
2036	Zr/PAA	T10	2 000		61	66	2,23
2031	-	T8	1 000	2,00	34 000	(naked tube)	
	-	T8	1 600 - 4 000	3,30-3,70-3,10	pretreating with silica (4 mg/ℓ)		
2031							
2031	-	T8	4 000	3,10	33 800	-	-
2032	Zr	T8	6 000	4,30	688	38	2,53
No Zr/PAA membrane prepared							

J. Membrane on Tube Pretreated with Hydrous Zirconia. Zirconia Treatment from 1 000 kPa to 4 000 kPa; Zr and Zr/PAA Membranes Formed at 6 000 kPa (Feed volume 100 ℓ).

Test	Membrane	Tube	Inlet pressure kPa	Cross-flow velocity m/s	Flux ℓ/m^{2}h	Rejection %	Conductivity of feed solutions mS/cm
2038	-	T6	1 000	2,00	13 800	(naked tube)	
2038	-	T6	1 000 - 4 000	2,80-4,30	precoating with hydrous zirconia		
2038	-	T6	4 000	4,30	3 360	-	-
2039	Zr	T6	6 000	4,30	636	41	2,54
2040	Zr/PAA	T6	6 000	4,30	165	82	2,43
2040	Zr/PAA	T6	3 000	4,40	57	80	2,47
2041	-	T4	1 000	2,40	42 500	(naked tube)	
2041	-	T4	1 000 - 4 000	2,40-3,30	precoating with hydrous zirconia (2 mg/ℓ)		
2041	-	T4	4 000	3,30	30 970	-	-
2042	Zr	T4	6 000	4,30	588	39	2,46
2043	Zr/PAA	T4	6 000	4,30	195	80	2,30
2043	Zr/PAA	T4	3 000	4,60	75	70	2,30

K. Membrane on Tube Pretreated with Hydrous Zirconia. Zirconia Treatment from 1 000 kPa to 4 000 kPa; Zr and Zr/PAA Membranes Formed at 4 000 kPa.

Test	Membrane	Tube	Inlet pressure kPa	Cross-flow velocity m/s	Flux ℓ/m^{2}h	Rejection %	Conductivity of feed solutions mS/cm
2044	-	T1	1 000	2,40	30 000	(naked tube)	
2044	-	T1	1 000 - 4 000	2,00-4,10	precoating with hydrous zirconia		
			4 000		10 673	-	-
2045	Zr/	T1	4 000	4,50	576	40	2,68
2046	Zr/PAA	T1	4 000	4,40	159	78	2,24
	Zr/PAA	T1	3 000	4,80	114	74	2,23
	Zr/PAA	T1	6 000	4,10	264	80	2,23
2050	-	T7	1 000	2,10	19 000	-	-
2050	-	T7	1 000 - 4 000	2,10-4,30	precoating with hydrous zirconia (2 mg/ℓ)		
		T7	4 000	4,30	3 940	-	-
2051	Zr/	T7	4 000	4,50	636	41	2,45
2052	Zr/IPS[*3]	T7	4 000	4,50	105	85	2,32
2052	Zr/IPS[*3]	T7	6 000	4,30	165	88	2,34

[*3] Co-polymer of polyacrylic acid and vinyl acetate.

APPENDIX 4

THE POTENTIAL OF DYNAMIC MEMBRANES FOR THE TREATMENT OF INDUSTRIAL EFFLUENTS

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THE POTENTIAL OF DYNAMIC MEMBRANES FOR THE TREATMENT OF INDUSTRIAL EFFLUENTS

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SYNPOSIS

Dynamic membranes for reverse osmosis or ultrafiltration have several advantages over conventional membranes for the treatment of industrial effluents. These advantages include the capability of their being operated at high temperature, the ease of replacement of the membrane in situ, long service life of the support tube and ability of the membrane to be operated on a feed without extensive pretreatment.

The formation of dynamic membranes and their application in treatment of a variety of industrial effluents is discussed.

INTRODUCTION

Membrane separation techniques have been developed over a number of years for desalination purposes, and, more recently, for the treatment of a variety of industrial effluents for water reuse purposes.

Industrial effluents often contain a wide range of chemicals including acids, bases, organics, colloidal material and suspended solids. Incompatibility of the membrane with the chemical nature of the effluent, temperature, and solids content often limit the selection of the membranes available and may make the use of extensive pretreatment of the effluent essential and expensive.

The use of dynamic membranes may overcome many of these problem areas. The advantages of a dynamic membrane include the following:

(i) long service life of the support tube.

(ii) ability to be operated at high pressure and temperature.

(iii) in cases of severe fouling, the membrane can be removed by chemical means and re-formed in situ.

(iv) solids removal, whilst always desirable, is not critical in terms of mechanical damage to the membrane.

FORMATION OF DYNAMIC MEMBRANES

Dynamic membrane technology was pioneered by the Oak Ridge National Laboratory[1,2]. Research indicated that membranes of the hydrous zirconium (iv) oxide type were more suitable than many of the other hydrous oxides which were tested.

Zirconium type membranes are formed by the deposition of hydrous zirconium (iv) oxide into the porous structure of the support by solution chemistry. Stringently controlled conditions are necessary for membrane formation.

Since stable zirconium chelate complexes form with many organic compounds by co-ordination through oxygen atoms, this enables the deposition of certain polymers onto the hydrous zirconium (iv) oxide. This in turn then leads to the possibility of tailoring a membrane for specific duties. The most commonly used polymers for this purpose are of the polyacrylic acid type.

The methods of formation are described in detail by Johnson et. al.[2].

It has been proposed[3,4] that when a dilute colloidal suspension of hydrous zirconium (iv) oxide, at a pH just below 4, is passed across the surface of a porous substrate, the first stage involves a pore filling, or bridging stage, where colloidal particles of hydrous zirconium oxide are captured on the walls of the porous support material. This process causes the pores to close after a period and is followed by a surface filtration 'cake' from colloidal particles, as commonly occurs in other types of cross-flow microfiltration. This then represents the hydrous zirconium oxide membrane, which in acidic solutions, is an anion exchanger.

When a polyelectrolyte, such as polyacrylic acid, is then passed over the hydrous zirconium (iv) oxide, the electrolyte enters the pores of the membrane rather than forming a gel layer on the surface. It is also suggested that at low pH values, the polyelectrolyte molecules are hypercoiled and easily able to penetrate and react with substrate. If the pH is then raised, the polyelectrolyte molecules expand to block the pores, thereby causing a rapid decrease in flux and increase in rejection. This then represents the composite (Zr/PAA) membrane, which in a neutral to alkaline solution has the properties of a cation exchanger.

The hydrous zirconium (iv) oxide membranes are characterized by high water fluxes whilst showing a significant salt rejection. The composite zirconium (iv)/polyelectrolyte membranes have lower water fluxes but significantly higher salt rejection capability. Actual values will depend on substrate and formation conditions of either the zirconium (iv) membrane or the composite membrane.

To distinguish these membranes from conventional detachable films prepared by casting or other procedures, the class is designated 'dynamically formed' or 'dynamic'.

Most early research was conducted using porous carbon or ceramic tubes for the support but problems with the robustness of the tubes limited the applicability of the research. Brandon and co-workers[5,6] used porous stainless steel as a support for dynamic membranes which overcame most of the problems associated with the carbon and ceramic tubes. The stainless steel tubes used in the work described in this paper were 14 mm inside diameter. The pore size was variable and the range was from 2 to 7 microns. Carre Inc. in their brochure[7] refer to the reliability of porous sintered stainless steel as the support material for high temperature dynamic membranes. Because of the material, high pressure operation is possible and single pass tubular dynamic membrane systems were developed. Such systems allegedly overcome some of the short-comings of other membrane systems. Such short-comings include prefiltration, low operating temperature, inefficient recirculation, tube breakage and capital expenditure for membrane replacement.

In our work on the use of such tubes, we have, however, found problems relating to the corrosion of the stainless modules under certain conditions. In general, however, the problem can be overcome by careful design of the modules and system and modification of the upstream process, where possible.

Hydrous zirconium (iv) oxide membranes and the zirconium (iv) polyelectrolyte membranes provide a range of salt rejections from 10 to over 95%. They have the following advantages for the treatment of industrial effluents:

1) high temperature stability.
2) long service life of the support tube.
3) the dynamic membrane is replaceable <u>in situ</u> by solution chemistry.
4) a range of dynamic membranes are available for tailoring to a particular application.
5) high flux rates.

Because the dynamic membrane is replaceable, fouling considerations are minimised and high strength industrial effluents may often be treated successfully.' However, if a component in the effluent has the potential to chelate with zirconium, then the choice of membrane may be the selectively prepared zirconium/polyelectrolyte membrane rather than a composite or dual layer membrane prepared randomly and fortuitiously by passage of the effluent over the zirconium (iv) oxide membrane. However, it should be recognised that this results in an initial lowering of the permeate flux.

INDUSTRIAL APPLICATIONS USING DYNAMIC MEMBRANES

Wool Scouring Effluent

Wool scouring produces an effluent considered to be among the most polluting of textile effluents. Typically the effluent contains 10 to 20 g/ℓ wool grease, 7 to 15 g/ℓ suint salts (salts produced by natural excretions) and 10 to 30 g/ℓ dirt (sand, vegetable matter and fibre). The chemical oxygen demand (COD) of the effluent can be as high as 50 000 mg/ℓ. Disposal of these effluents at present is mainly by solar evaporation which has become unacceptable due to environmental considerations.

A first consideration in the treatment of wool scouring effluent was to slightly modify the wool washing process to produce two effluent streams[8], one containing mostly the dirt and suint loading, (1 kℓ/h) the other containing the grease loading (3,2 kℓ/h). The low volume stream has been successfully treated by falling film evaporation.

Initial research using conventional ultrafiltration membranes to treat the grease effluent showed these membranes to be unsuitable for wool scouring effluents, the characteristics of the effluent being such that permanent damage to membrane occurred within a very short space of time.

Laboratory scale experiments and subsequent pilot plant trials at a South African wool scouring company indicated that dynamic membranes of the hydrous zirconium oxide type could be used successfully to treat the effluent with an 85% water recovery. The membrane system was capable of rejecting 92 to 96% of total organic carbon and 85 to 90% of the total solids. Grease rejection was 100%.

A plot of flux versus water recovery is shown in Figure 1.

As a result of the pilot plant results, it was decided to construct a modular demonstration plant at a wool scouring factory to treat desuinted wool scouring effluent. The demonstration plant is coupled to one of the factory scouring trains, and incorporates a liquor recirculating system with sludge withdrawal, and a dynamic membrane ultrafiltration plant. The permeate is recycled to the scouring train.

The dynamic membrane plant uses porous stainless steel tubes as the support for the membrane. A module, which is 3,5 m long and 215 mm in diamter, contains 150 m of 14 mm ID porous stainless tubes, the total porous area of which is 6,8 m^2. A total of 10 modules is in use to treat the effluent from one scour line.

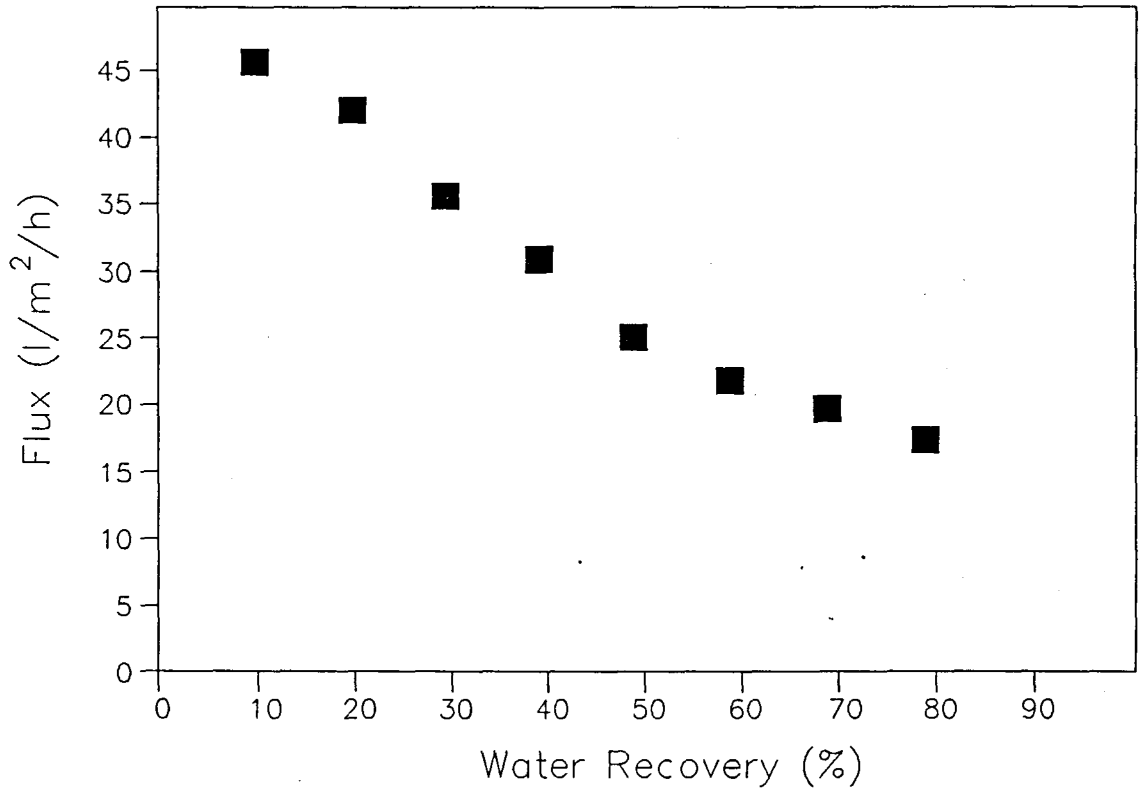

FIGURE 1 : Wool Scouring Effluent:
The Effect of Water Recovery on Permeate Flux

The demonstration plant has been operating as a factory production unit for approximately five months. During this operating period, the need for membrane re-formation has been demonstrated as modules have become fouled. Remembraning has been accomplished by chemically cleaning the fouled membranes to a bare tube state and re-forming the membrane.

Dynamic membranes have thus proved to be able to operate under conditions in which conventional membranes have thus far not proved to be successful.

Textile Soaping Effluent

Textile soaping effluents are produced in a cleaning process after the continuous dyeing and printing of cloth. The effluents are hot (90°C) and contain dissolved and colloidal dyestuffs, detergents and some salts. Considerable savings in heat energy are possible, if the clean permeate is returned to the process at or near the operating temperature. Dynamic membranes afford the possibility of operating at this temperature.

Extensive laboratory trials have been conducted on effluent from a particular textile mill, the results of which are summarised in Table 1.

These laboratory trials were conducted at a temperature of 50°C and operating pressure of 4 MPa. Large dynamic plants can be designed to operate at higher temperatures, and 6 MPa operating pressure. It is anticipated therefore that membrane fluxes can be improved significantly for commercial operation.

TABLE 1 : Dynamic Membrane Treatment of Textile Soaping Effluent

	Feed concentration			Overall permeate conc. at 90% water recovery			Membrane flux
	TDS mg/ℓ	TOC mg/ℓ	ADMI Colour units	TDS mg/ℓ	TOC mg/ℓ	ADMI Colour units	ℓ/m^2h
Average	2 070	705	1 265	850	240	51	55,4
Maximum	5 060	1 270	3 550	1 470	545	105	168
Minimum	620	142	430	230	45	20	30

TDS = total dissolved solids.
TOC = total organic carbon.
ADMI = American Dye Manufacturers Institute.

Effluents from Viscose/Polyester Dyeing

The standard approach to textile effluent treatment has been extensively researched by organisations such as the Environmental Protection Agency, USA. The proposed treatment involves biological oxidation followed by operations such as flocculation, settling, filtration, carbon adsorption, ozonation, resin adsorption, ion exchange, reverse osmosis, hyperfiltration and electrodialysis. The characteristics of effluent, however differ with mills and processes. Textile effluents containing colloidal dyestuff are difficult to treat by biological systems and are not decolourized effectively by activated carbon adsorption or ozonation. One of the most promising techniques for the treatment of dyehouse effluents has been shown to be the use of a membrane separation process[9,10] as it is a one step process and gives good removal of salt, organics and colour.

The effluent from any mills' dyehouse is a function of the major fibre utilized by the mill because the techniques employed during the processing of any fibre are fairly universal. Viscose tends to be dyed with direct, vat or reactive dyes by methods essentially the same as for cotton giving a similar effluent. The dyeing system for polyester is simple. The disperse dyes are applied to the fibre at temperatures up to 130°C in the presence of some dispersing/levelling agent.

The effluents from the various dyeing systems vary as follows:

Direct dyes:	pH	neutral 6,5 to 7,5
	Temperature	60 to 100°C
	Colour	low
	TDS	very high, 200 g/kg cloth.
Reactive dyes: (exhaust method)	pH	highly alkaline >11
	Temperature	60 to 100°C
	Colour	Fairly high, depending on depth of shade
	TDS	extremely high, >900 g/kg cloth.
Reactive dyes: Cold batch	pH	highly alkaline >11
	Temperature	50°C
	Colour	high
	TDS	10 to 25 g/kg cloth.
	(use of sodium silicate optional; effect is to reduce fixation time).	
Vat dyes:	pH	highly alkaline >11
	Temperature	20 to 90°C
	Colour	high
	TDS	very high, 145 to 355 g/kg cloth.
Disperse dyes:	pH	4,5 to 5,5
	Temperature	120 to 130°C
	Colour	Low, except in dark shades
	TDS	Variable, dependent on shade.

The viscose/polyester dyeing effluent thus contains both soluble and colloidal dyestuffs, acetate, alkali, salt and organic auxiliary chemicals. Processing conditions result in an effluent varying in pH from 4 to 9, with temperature up to 75°C and total dissolved solids up to 4 500 mg/ℓ. The colour in ADMI units can be above 10 000.

A typical example of a viscose/polyester dyehouse effluent from a textile finishing and dyeing mill was investigated. The effluent varies depending on the current dyeing process but generally has a pH of between 7 and 9 and is high in chemical oxygen demand (COD) with a dark colouring. This effluent was being discharged to sewer but became a problem as it was affecting the biological performance of the sewerage works and subsequently polluted the river to which the sewage works discharged. The textile effluent was a high proportion of the total flow to the sewage works.

Tests on this effluent using a membrane separation process showed that up to a water recovery of 70% the overall permeate quality was suitable for use as process water in dyeing. The composite permeate produecd at a 90% water recovery can be used for certain washing processes. Given in Table 2 are results at 90% water recovery.

TABLE 2 : Comparison Between Feed and Overall Permeate at 90% Water Recovery

Feed			Permeate		
Conductivity mS/cm	TOC mg/ℓ	ADMI Colour units	Conductivity mS/cm	TOC mg/ℓ	ADMI Colour Units
0,62	142	430	0,23	45	20
2,07	705	1 265	0,85	240	51
5,06	1 270	3 550	1,47	545	105

Composite Zr/PAA membranes were also tested and the results after batch concentrations are shown in Table 3 for two types of viscose/polyester dyeing effluent.

TABLE 3 : Batch Concentration of Viscose/Polyester Effluents Using Zr/PAA Membranes

		Test A		Test B	
		Initial Feed	Rejection %	Initial Feed	Rejection %
ADMI	(Colour units)	2 025	99	3 400	99
TOC	(mg/ℓ)	-	-	430	97
TDS	(mg/ℓ)	300	50	1 300	93
pH		4,3		8,5	
Flux (at 4 MPa)	(ℓ/m^{2}h)		130 to 50		115 to 56
Water recovery	(%)		70		70

In a third test on mixed effluents at pH values of 7,8 to 9,3 an overall water recovery of 80% was achieved. Rejections were similar to results in Test B and the flux ranged from 98 to 50 ℓ/m^{2}h.

These preliminary investigations demonstrated the versatility of the composite dynamic membrane where processing conditions varied with temperatures up to 75°C, pH values of 4,3 to 9,3 and feeds with both soluble and colloidal dyestuffs and total dissolved solids and colour rising to 4 500 mg/ℓ and 10 000 ADMI units

Since the effluent is hot (dyeing taking place at 130°C for the polyester component of the fabric) the possibility exists for significant heat energy savings if such effluent can be treated on a closed loop recycle basis. Because of the high temperature and fibre/suspended solids content of such effluents, the use of dynamic membranes on porous stainless steel tubes was again considered.

An ultrafiltration plant was installed at the mill about 4 years ago. At that stage it was believed to be one of the biggest of its type in the world with a total membrane area in the region of 280 m^2. The plant employs a closed loop system with the permeate being reused in the dyehouse and the reject being sent to an evaporator. Whilst the membranes were capable of rejecting the deleterious components from the effluent so as to make the permeate suitable for reuse in the dyehouse there were some shortfalls in the design of the plant.

Two of the major problems existing at the ultrafiltration plant are the low fluid velocity past the membranes and the stagnant conditions which develop in some areas of the membrane separation modules. These conditions have led to severe fouling and corrosion problems which have obviously adversely affected the performance of the plant.

Although the plant is still operating, it is currently being refurbished with a view to improving the flux/rejection characteristics of the plant and solving the problems of fouling and corrosion.

Dilute Acrylic Emulsion Effluent

An example of this type of effluent is the one produced by a local factory that manufactures a range of acrylic polymers. The effluent is produced during high pressure water cleaning of the polymer reaction vessels after the batch production of polymers. The effluent is milky in colour, has a high total organic carbon content and contains a foaming agent. The foaming agent first alerted the municipal authorities to the effluent which was suspected of overloading the borough sewerage works.

Several processes were investigated to treat the effluent and to reduce the concentration of surfactants. These included flocculation involving various flocculants and the subsequent removal of the foaming agent by adsorption on carbon and resins. These methods met with limited success.

It was decided to investigate the use of membrane separation and so develop a closed loop system where the effluent could be recycled in the washing of the polymer reaction vessels. After preliminary trials using membrane separation techniques, a small scale plant was established and proved initially successful in treating the effluent. The membranes gave a near 100% colloidal rejection, thereby eliminating all milkiness, and a 90% rejection of total organic carbon. Although the permeate contained some foaming agent it was acceptable for reuse in the washing process.

During the early full scale plant tests the membranes used for treating the effluent were of the hydrous zirconium (iv) oxide membrane type. Because of the nature of the effluent it soon became evident that a hydrous zirconium (iv) membrane was not suitable for treating an effluent of this type. Present in the effluent are a considerable number of various polymers and co-polymers as a result of the washing process. There are also limited quantities (parts per million) of some monomers and short chain polymers present. Some of these organic polymer species react with the hydrous zirconium (iv) oxide membrane and a secondary membrane is formed. Although this secondary membrane has no detrimental effect with regard to rejection of the colloids and carbon components, it reduces the flux considerably.

These randomly and fortuitously formed secondary membranes were exceptionally difficult to clean or strip and for this reason it was decided to go the way of a composite membrane formed from a known polymer, such as polyacrylic acid of known molecular mass. The advantages of this type of membrane are that all the active sites present on the hydrous zirconium (iv) membrane have been taken up by the polyacrylic acid (PAA). We then have a membrane that is inert with regard to reaction with the random species present in the effluent.

With regard to rejection, the Zr/PAA composite membrane exhibits good colour and total organic carbon rejecting characteristics i.e. 100% colloidal matter (milkiness) and over 90% total organic carbon. The flux capabilities of this membrane are, however, somewhat lower to start with, but are more stable than the fluxes obtained with what is initally only a hydrous zirconium (iv) oxide membrane. The reason for there being significantly less flux decline is due to the fact that there is little or no chemical reaction between the Zr/PAA membrane surface and the effluent. The membrane is therefore more responsive to cleaning methods, and removal of the fouling layer will restore the flux capabilities of the membrane. The hydrous zirconium (iv) oxide/polyacrylic acid membrane is also more readily stripped from the substrate than the randomly formed membranes produced from various polymers/co-polymers in the effluent. This then enables more rapid stripping of the composite membrane for remembraning the support when required.

CONCLUSIONS

Dynamic membrane technology has shown that membrane separation techniques can be applied in the variety of harsh conditions associated with industrial effluent treatment.

Development of a membrane suited to each particular process should be regarded as an important part of the research as each specific process fluid may have a different interaction with the membrane surface.

The economics of a dynamic membrane plant have to be carefully planned with regard to the savings in operating expenses such as heat energy and membrane replacement costs, versus the lower costs of a conventional membrane plant with the built-in running expenses of membrane replacement and costly pretreatment.

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APPENDIX 5

DYNAMIC MEMBRANE TREATMENT OF WOOL SCOURING EFFLUENT

The Symposium on Advances in Reverse Osmosis and Ultrafiltration

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Pollution Research Group
Department of Chemical Engineering
University of Natal
Durban

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DYNAMIC MEMBRANE TREATMENT OF WOOL SCOURING EFFLUENTS

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Wool scouring effluent contains up to 33 g/ℓ total solids, 21 g/ℓ emulsified grease and 7 g/ℓ suint salts and the discharge of this effluent with a COD of 30 g/ℓ, places severe restrictions on the siting of wool washeries. Investigations into the treatment of this effluent have resulted in the construction of a modular demonstration plant utilising hydrous zirconium oxide membranes on sintered stainless steel tube supports. The permeate is recycled to the scouring process. The design capacity of the plant is 3,2 m^3/h. The chemistry of dynamic membrane formation is described together with design and operational details of the plant.

Introduction

Wool scouring effluents are heavily polluted with the impurities from greasy wool; grease, suint and dirt. Grease wool varies in yield of clean wool from 40% to 75% and contains from 5 to 40% grease, 2 to 20% suint salts and 5 to 40% dirt and moisture (1). During scouring these impurities are removed resulting in a highly contaminated effluent. Scouring is carried out at 50 to 70°C with nonionic detergents and builders such as sodium carbonate. Typically five bowls make up each scouring train, the volume of each bowl being 8 to 11 m^3. Counter-current scouring is the most commonly used method of operation with clean water entering the last bowl, which is used for rinsing, and then flowed backward towards the first bowl. Detergent, builder and steam are added to the scouring bowls. The detergent consumption is determined by the impurity load on the grease wool. Typical usage figures are:-

process water	5 to 15 ℓ/kg grease wool.
detergent	3 to 10 g/kg grease wool.
sodium carbonate	8 to 12 g/kg grease wool.
steam (heating and drying)	2 to 5 kg/kg grease wool.

The effluent loads are determined from the clean wool yield. The average yield is about 55% with the mass of grease-suint-dirt impurities in the ratio 1 : 0,6 : 1,4.

At a water usage of 10 ℓ/kg grease wool the effluent composition would be 15 g/ℓ grease, 9 g/ℓ suint salts and 21 g/ℓ dirt.

Wool-grease is composed of a mixture of large numbers of water insoluble alcohols and higher fatty acids combined to form esters. Suint is the water soluble constituents of the fleece and is a complex mixture of inorganic ions and organic acids along with urea and colouring materials (2). The main inorganic component is potassium and the acids include acetic, propionic, butyric, valeric, succinic and glycollic. The dirt fraction includes sand and mud, vegetable matter and skin scurf.

The effluent decomposes readily giving a progressively disagreeable odour. The putrification is associated with the suint and to a lesser extent to the sludge and wool fibre; the grease itself is relatively stable. The grease can be recovered as a saleable by-product, lanolin.

High yielding wool qualities produce relatively low pollution load effluents and a high quality (unoxidised) grease whereas low yielding wool qualities produce high load effluents with low quality (oxidised) grease. In addition, the emulsified grease droplets are associated with significant quantities of dirt particles. Whereas established techniques such as acid cracking, centrifugation and flotation can recover grease from the effluent, the resulting product is not suitable for reuse because of the high suint load (3,4).

The treatment of normal wool scouring effluents, to reuse standard, would involve grease separation, removal of dirt and then separation of the suint salts from the water. Grease and dirt can be removed by ultrafiltration and partially by centrifugation and flotation. Removal of the suint salts would involve the additional process of reverse osmosis or evaporation. In order to overcome the inherent disadvantages of treating conventional scouring effluent, a modified desuint scouring system was introduced (3,5).

The purpose of the system was to:-

(a) remove suint and dirt in a cold desuinting bowl (Bowl 1) at low water usages. The removal of high percentages of the suint load enables water reuse of the scouring effluent to be more easily attained. This is achieved by reducing the salt load to the scour effluent treatment section thus limiting the salt build-up in the recycling process.

(b) the desuinting effluent is treated by settling and then by reverse osmosis or evaporation to produce reusable permeate or condensate and a crude potassium-suint fertilizer concentrate.

(c) detergent scouring is carried out in the normal way in three bowls (Bowl 2, 3 and 4) to produce an effluent with relatively lower concentrations of dirt and suint. This effluent is treated by ultrafiltration to produce a reusable permeate and a grease/dirt concentrate which is treated in the centrifugal grease recovery plant where three streams are produced (aqueous, sludge and grease). The aqueous stream is returned to the ultrafiltration plant.

(d) The last bowl (Bowl 5) is a cold water rinse. The overflow from this bowl is used as make-up for the desuint and scouring sections.

(e) Side settlers were introduced on the desuinting and first scouring bowls to control the solids build-up in the bowls by removing the readily settleable solids. This reduces the frequency of interruptions for cleaning thereby increasing scourline utilisation and reducing water usage.

Previous investigations had indicated that conventional ultrafiltration membranes were prone to fouling and physical damage due to the presence of the colloidal dirt particles (6). Dynamic (formed in place) membranes of hydrous zirconium (iv) oxide on tubular sintered stainless steel supports have been shown as to be suitable for treating desuinted wool scouring effluent (7).

Advantages of such a system are:-

(i) high temperature operation (60°C).

(ii) robust membrane is not physically damaged by the dirt particles.

(iii) mechanically strong system hence high pressure (6 MPa) operation can be employed.

(iv) tubular configuration (14 mm inside diameter) reduces the potential for physical blockage.

(v) the membranes can be subjected to relatively severe cleaning procedures.

(vi) the membranes can be stripped and replaced when they have become excessively fouled.

Dynamic Membranes

Dynamically formed membranes were produced by a research group at Oak Ridge National Laboratory (ORNL) in the USA. Such membranes are formed *in situ* when a dilute solution (10^{-4} molar) of one or more specific additives is passed over the surface of a porous support (8).

The most promising membranes which have been developed are the hydrous zirconium (iv) oxide membrane and the hydrous zirconium (iv) oxide-polyacrylic dual layer or composite membrane (8,9).

Some Characteristics of Zirconium. Zirconium and hafnium always occur together in nature and because they have very similar properties, their separation is both difficult and expensive. For most practical applications, other than atomic energy, the hafnium is thus not separated from the zirconium (10).

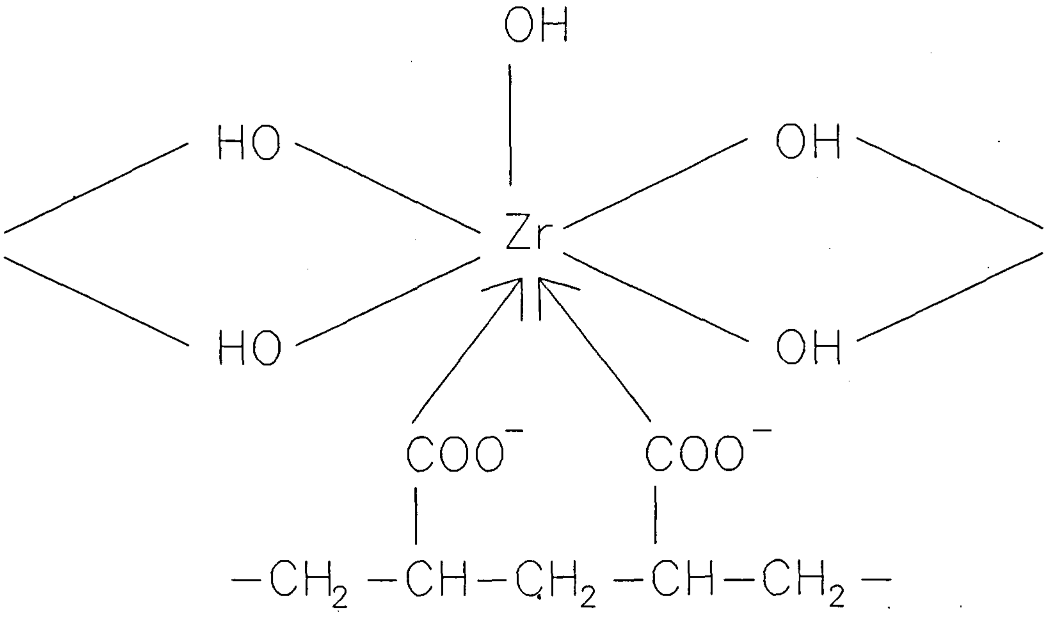
The zirconium nitrate solutions used in the work described in this paper were prepared from zirconium basic carbonate by treatment with 93 to 95% nitric acid. The resulting zirconium nitrate salt would contain about 2% hafnium.

Zirconium (iv) species are polymerized in aqueous solutions. The increasing polymerization with decreasing acidity can be followed readily by light scattering studies. It can be shown that at concentrations from as low as 10^{-4} molar zirconium, a colloid phase exits at pH values as low as 3. Once formed, the colloid will not readily revert to a soluble form even when the pH is reduced to pH 2,0.

The zirconium polynuclear hydroxy species can be cationic, anionic or neutral and this is important in the subsequent use of the hydrous oxide.

The ability of zirconium to react strongly with oxygen containing species has led to the increasing use of zirconium-organic polymer systems. At least two (-OH) groups or at least one (-CO-) radical as an aldehyde or carbonyl group or a polypeptide link (-CO-NH-) should be present.

A well known chelate complex of zirconium and polyacrylic acid may be shown as follows:



This reaction is used in forming the classic dual layer or composite Zr/PAA dynamic membrane (8,9).

<u>Model for Formation</u>. It has been proposed that when a dilute colloidal suspension of hydrous zirconium oxide, just below pH 4, is passed across the surface of a porous substrate, the first stage involves a "pore filling" or a bridging stage where colloidal particles of the hydrous zirconium oxide are captured on the walls of the pores of the support material. This process causes the pores to close after a period and is followed by the formation of a surface filtration "cake" from colloidal particles as commonly occurs in other types of cross-flow microfiltration. The membrane so formed represents the hydrous zirconium oxide membrane which, in acidic solution, has anion exchange properties.

When a polyelectrolyte such as polyacrylic acid is then passed over the hydrous zirconium (iv) oxide, the electrolyte enters the pores of the membrane rather then forming a gel layer on the surface. It is also suggested that at low pH values; the polyelectrolyte molecules are hypercoiled and easily able to penetrate and react with the substrate. If the pH is then raised, the polyelectrolyte molecules ionise and expand to block the pores thereby causing a rapid decrease in flux and an increase in rejection (11,12). This then represents the composite membrane, which in neutral to alkaline solution has the properties of a cation exchange.

The hydrous zirconium (iv) oxide membranes are characterized by a high water flux while showing a significant salt rejection. The composite zirconium/polyelectrolyte membranes have a lower a water flux but a significantly higher salt rejection capability.

To distinguish these membranes from conventional detachable films prepared by casting or other procedures, the class is designated "dynamically formed" or "dynamic".

Selection of Porous Support. Most early research was conducted using porous carbon or ceramic tubes for the support, but problems with the robustness of the tubes limited the applicability of research.

Brandon *et. al.* and Mott *et. al.* used porous stainless steel as a support for dynamic membranes which overcame most of the problems with the carbon and ceramic tubes (13,14).

Carre Inc. in their brochure refer to the reliability of porous stainless steel as the support material for high temperature dynamic membranes (15). Also, because of the material, high pressure operation is possible and thus single pass tubular dynamic systems were developed.

Such systems overcome some of the shortcomings of other membrane systems. Such short comings include extensive prefiltration, low operating temperature, inefficient reticulation, tube breakage and capital expenditure for membrane replacement.

In our work on the use of such tubes, however, we have found problems relating to the corrosion of the stainless steel modules under certain conditions. In general, however, the problem can be overcome by careful design of the modules and system and, where possible, modification of process.

Hydrous zirconium (iv) oxide membranes and the zirconium (iv) polyelectrolyte membranes provide a range of salt rejections from 10 to over 95% and in the treatment of industrial effluents they have the following advantages:-

(i) high temperatures stability

(ii) long service life of the support tube.

(iii) the dynamic membrane is replaceable *in situ* by solution chemistry.

(iv) a range of dynamic membranes are available for tailoring to a particular application.

(v) high flux rates.

Because the dynamic membrane is replaceable, fouling considerations are minimised and high strength industrial effluents may often be treated successfully. However, if a component in the effluent has the potential to chelate with zirconium, then the choice of membrane may be the selectively prepared zirconium/polyelectrolyte membrane rather than a composite or dual layer membrane prepared randomly and fortuitously by passage of the effluent over the zirconium (iv) oxide membrane.

Cleaning Procedures and Membrane Removal Procedures. In normal operation, the membrane in any membrane separation module can become fouled by mineral scale, biological matter, colloidal particles and insoluble organic constituents. Deposition builds up on the membrane surfaces during operation until they cause loss in permeate output or loss of salt rejection or both. In addition, some chemicals react with the membrane surface producing a secondary membrane; in the case of zirconium (iv) oxide membranes chelation with oxygen containing compounds may result in a secondary membrane.

The fouling layer which has been deposited can be removed by various cleaning solutions containing, for example, enzymes, detergents, nitric acid, caustic soda, hydrogen peroxide, fluoride etc. These solutions must however be carefully selected to avoid damage to the membrane.

In the case of the hydrous zirconium (iv) oxide membrane, acid solutions of molar concentration greater than 0,1 must be avoided. In the case of composite membranes such as Zr/PAA, the use of hydrogen peroxide in solutions at pH values as low as 8 should be avoided since not only will the chelated polyelectrolyte be removed but so also will the hydrous zirconium (iv) oxide component of the composite membrane.

The hydrous zirconium (iv) oxide membrane alone, however, is not affected by H_2O_2 until pH values near 10.

Damage to the stainless steel substrate must, of course, also be carefully guarded against. This would eliminate all use of chloride and fluoride containing cleaning solutions.

Stripping of Membranes from Substrate. Stripping of membranes from the substrate can be achieved quite readily and would be done when fouling has become excessive and cleaning methods no longer effective.

The most satisfactory stripping of either hydrous zirconium (iv) oxide or a Zr/polyelectrolyte membrane has been found to be hydrogen peroxide in 1 molar caustic soda solution, followed by nitric acid (1 molar). Such cleaning can be done best by slow circulation of the respective solutions through the tubes.

After cleaning, the membranes can be redeposited in the standard manner and the membrane separation process recommenced.

Pilot Plant Results

A factory scouring line was modified to produce separate desuint, scouring and rinsing effluents (16). The modified line was used to produce over 2 million kg of scoured wool of various grades. The quality of the scoured wool was not adversely affected by the modification to the scour line nor by any recycle trials.

The implementation of the modifications has resulted in an increase in scoured wool throughput, a reduction in scouring effluent volume (20 m^3/week), a total effluent reduction of 85 m^3/week and savings in detergent, steam and sodium carbonate. The installation of the settlers resulted in the removal of 47% of the total incoming solids and assisted in controlling the solids build-up in the bowls and thus reducing the cleaning frequency.

A falling-film pilot evaporator (100 to 200 ℓ/h condensate) was operated for three months on the desuint effluent. Feed concentrations of 30 g/ℓ to 600 g/ℓ total dissolved solid were investigated. There was minimal fouling of the heat exchange surfaces. Cleaning was accomplished using dilute nitric acid at 80°C. The quality of the condensate was acceptable for reuse in the rinsing section of the scour line although the characteristic odour of wool scouring effluent was still present. No foaming was noted.

A pilot plant with a total membrane area of 25 m^2 was used to treat the scour effluent. The hydrous zirconium (iv) oxide membranes were formed on 16 mm ID sintered stainless steel tubes supplied by Mott Inc., Newmet Inc. and Carre Inc. The inlet pressure to the system was 4 to 5 MPa. A partial feed and bleed mode of operation was used to concentrate the effluent over a period of about 14 days. The rejection of grease was 100% while the point rejection calculated using conductivity, total solids and total carbon were 50 to 60, 85 to 90 and 95% respectively. The rejection was found to be relatively insensitive to feed concentration. The permeate flux was found to be a strong function of feed total solids and degree of fouling but was relatively insensitive to pressure. The permeate flux was stabilised by a chemical clean, using hydrogen peroxide at pH 8,0 to 8,5, for 30 to 60 minutes every 24 to 48 hours. The flux data shows a lot of scatter but a reasonable flux: total dissolved solids correlation (at 50 to 60°C) was:

$$J = 50 - 0,18 TS$$

where J = permeate flux (ℓ/m^2h).
TS = total solids concentration (g/ℓ).

For a feed at a total solids concentration at 30 g/ℓ the point flux would be 45 ℓ/m²h. The average flux for a batch concentration (85% water recovery) would be 37 ℓ/m²h.

Demonstration Plant Design

The decision to design and build a modular demonstration plant was based on the following needs:-

(i) to demonstrate the technology to the wool scouring industry and pollution abatement agencies,

(ii) to transfer the technology from an academic research organisation to an engineering consultant.

(iii) to obtain realistic cost data for the process.

(iv) to obtain long term operational and performance data.

The simplified process flow diagram is shown in Figure 1. Although modern scour lines were available which incorporated features such as low bowl volume, high contaminant exchange efficiencies and low liquor ratios it was decided to couple the modular demonstration plant to an old scour line for the following reasons:-

(i) there are many such scour lines in operation in the world.

(ii) this type of scour line can handle all grades of wool and in particular is well suited to low yielding wool (i.e. high strength effluent).

(ii) if the process performance is satisfactory on this type of equipment and low yielding wool then the system would be capable of treating high yielding wool grades scoured on modern equipment.

Since the factory consists of many scouring lines and any effluent treatment plant would be installed over an extended period of time, it was considered acceptable to delay the installation of the evaporator (for the desuint effluent) and the reverse osmosis plant (for part of the ultrafiltration permeate). Because of wool quality and production considerations it is expected that each scour line would be coupled to an ultrafiltration plant whereas the evaporator and the reverse osmosis plant would treat a combined factory stream.

The mass balance for the two cases (with and without reverse osmosis and evaporation) are shown in Figures 2 and 3. The design basis (worst case) is given in Table I.

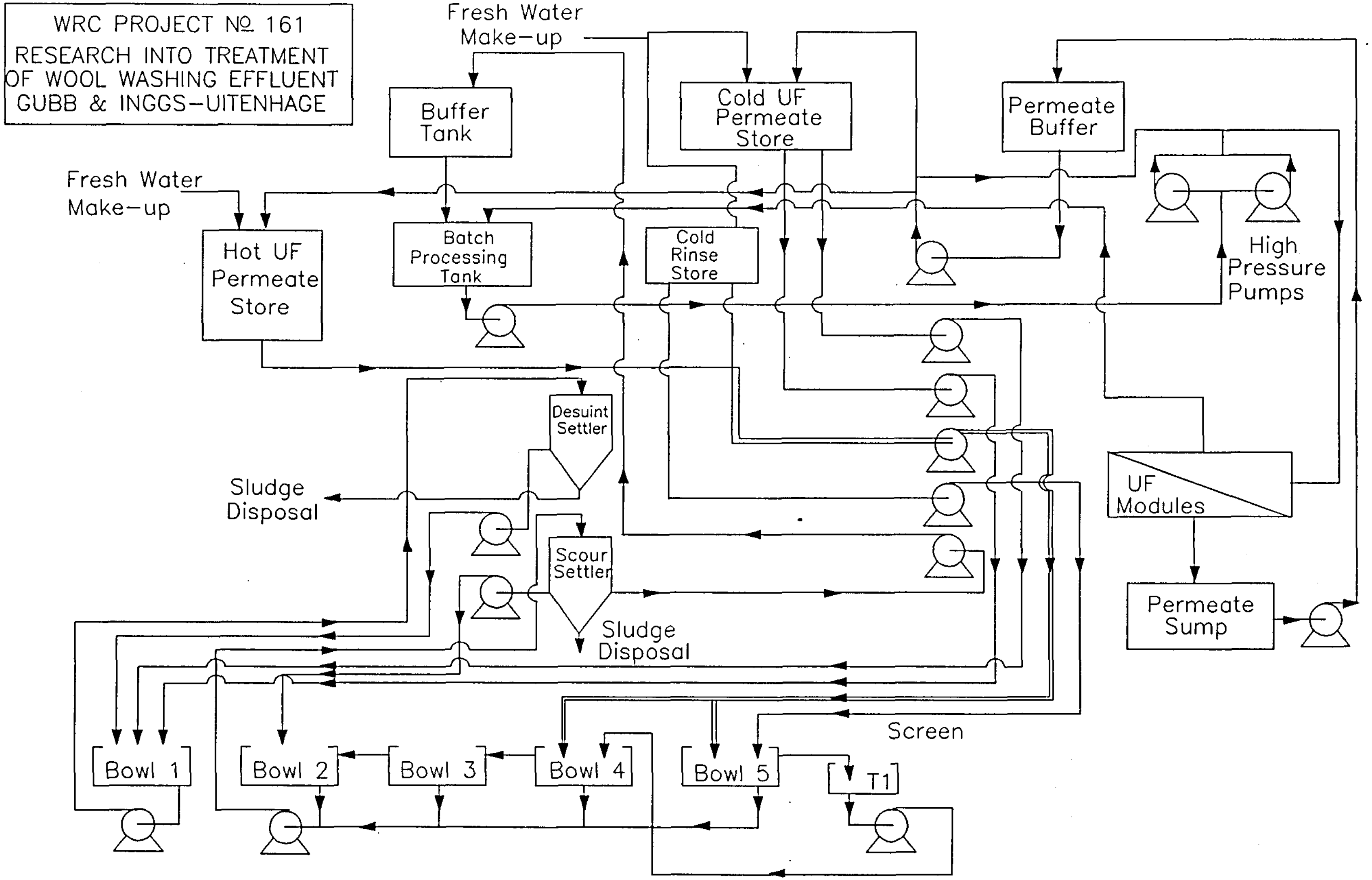


FIGURE 1 : Simplified Schematic Diagram of Modular Treatment Plant Showing only Main Process Lines

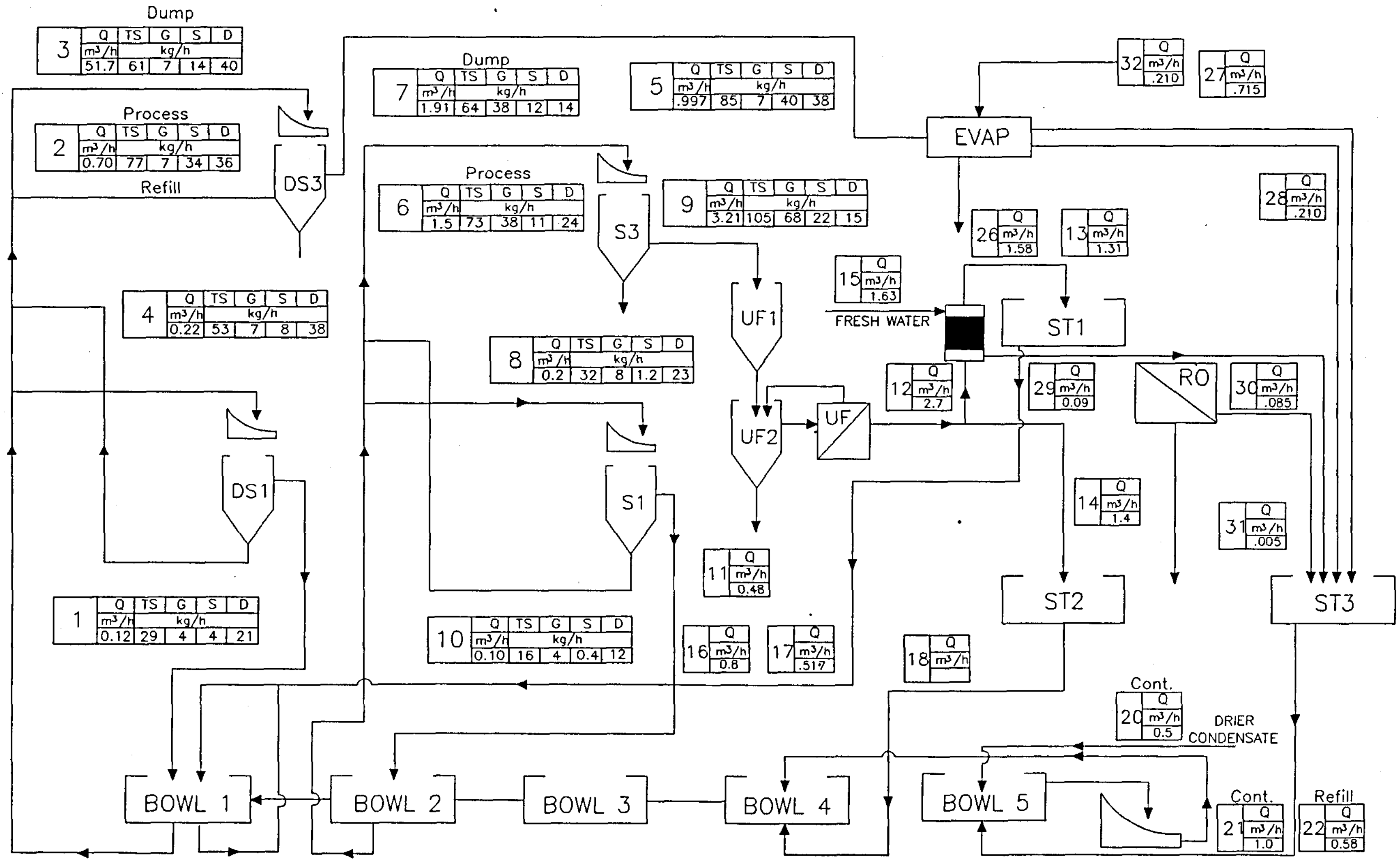


FIGURE 2 : Process Flow with RO and Evaporator

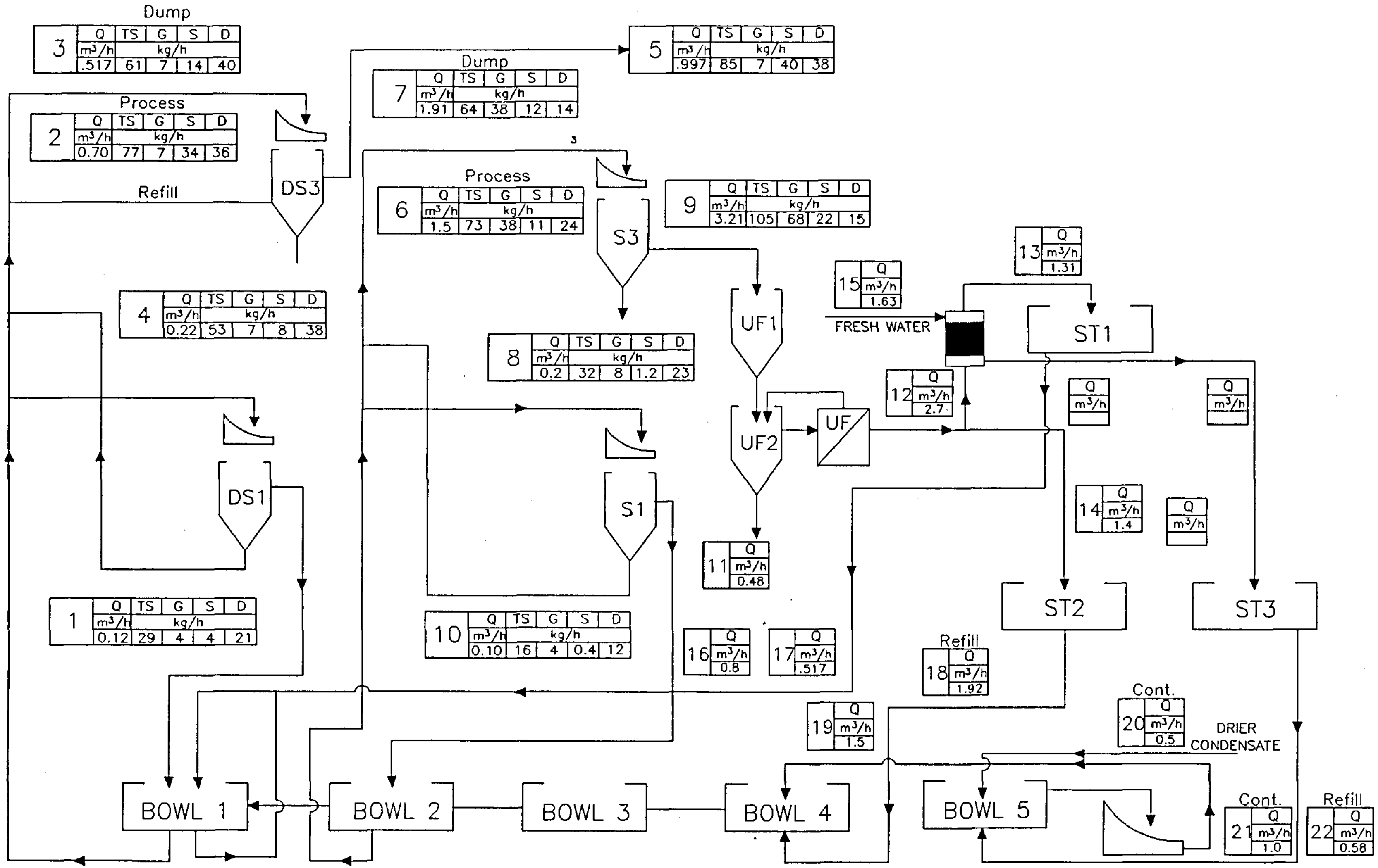


FIGURE 3 : Process Flows without RO and Evaporator

TABLE I : Ultrafiltration Plant Design Basis

Effluent flow	3 217 ℓ/h
Total solids	32,9 g/ℓ
Grease	21,1 g/ℓ
Suint	7,1 g/ℓ
Dirt	4,7 g/ℓ
Temperature	50 to 65°C
Water recovery	85%
Permeate flow	2 737 ℓ/h
Nominal module area	7,2 m^2
Number of modules	10
Module configuration	6 : 4
Inlet pressure	5 MPa
Inlet velocity	2,0 m/s

The scour effluent is screened to remove fibre and then passes into a settling tank to remove particulates. The settler also serves as a balancing tank and the supernatant liquor is removed through a floating discharge. The settled scour effluent is batch concentrated in the ultrafiltration plant. The water recovery (85%) is set using level probes. At the end of each batch concentration the concentrate is discharged to the centrifugal grease recovery plant. Air is injected into each of the ultrafiltration modules in order to displace as much of the concentrate as possible prior to the commencement of the flushing and cleaning cycle. A variety of cleaning chemicals can be added to the permeate (which contains detergent and has a pH of 8,5 due to the sodium carbonate) in order to clean the membranes. Cleaning continues during the concentrate draining period and the feed tank recharging period. It is suspected that while the cleaning solution helps maintain satisfactory permeate flux rates, it slowly degrades the membrane.

In view of corrosion problems which were experienced on another application of dynamic membrane technology, the porous stainless steel tubes are immersed in open troughs. The supports are inspected and cleaned daily. The troughs also serve as tanks for cleaning chemicals when the modules are being stripped prior to membrane formation. The modules are disconnected from the scour effluent system and the cleaning solutions are circulated through the tubes under low pressure and flow conditions.

The tubular modules are operated in a batch concentration mode because the variation in the effluent composition and the decrease in permeate flux with concentration makes the hydraulic design of a once through or series taper plant extremely difficult.

Results

The zirconum membranes were formed on the porous supports at the University and then transported to the wool scouring factory where they were stored for a period of about one month. After 7 modules were installed on the plant water fluxes were measured using untreated local tap water as feed. The permeate fluxes were very much lower than the fluxes obtained directly after membrane formation in which reverse osmosis permeate was used as the test solution. The test conditions were:

Inlet pressure	5 MPa
Outlet pressure	4 MPa
Velocity	1,5 m/s
Temperature	40°C.

Comparative fluxes are given in Table II.

Previous experience has indicated that the membrane flux performance does not change significantly on storage. It is suspected that the poor quality of the local tap water was the cause for the reduction in membrane water flux

TABLE II : Comparative Water Fluxes

	Module Number						
	1	2	3	4	5	6	7
Flux on formation (ℓ/m^2h)	400	380	400	450	470	500	470
Flux on commissioning (ℓ/m^2h)	38	45	59	50	50	48	50

In spite of the fact that the modules had similar fluxes after membrane formation and on initial testing on the pilot-plant, after exposure to the effluent there was a wide range in permeate flux e.g. at 50% water recovery the highest flux module produced 32 ℓ/m^2h while the lowest flux module produced 17 ℓ/m^2h. This trend was maintained for different feed concentrations over a period of 3 months. After the institution of regular peroxide cleaning cycles at the completion of each batch concentration, all but one of the modules exhibited a significant increase in permeate flux. The flux declined slowly over a period of 1 month and remembraning of all the modules has had to be undertaken (Figure 4). The membrane rejection has been satisfactory during the complete period of operation. In future it is planned to strip and reform the membranes on a rotational basis at the factory.

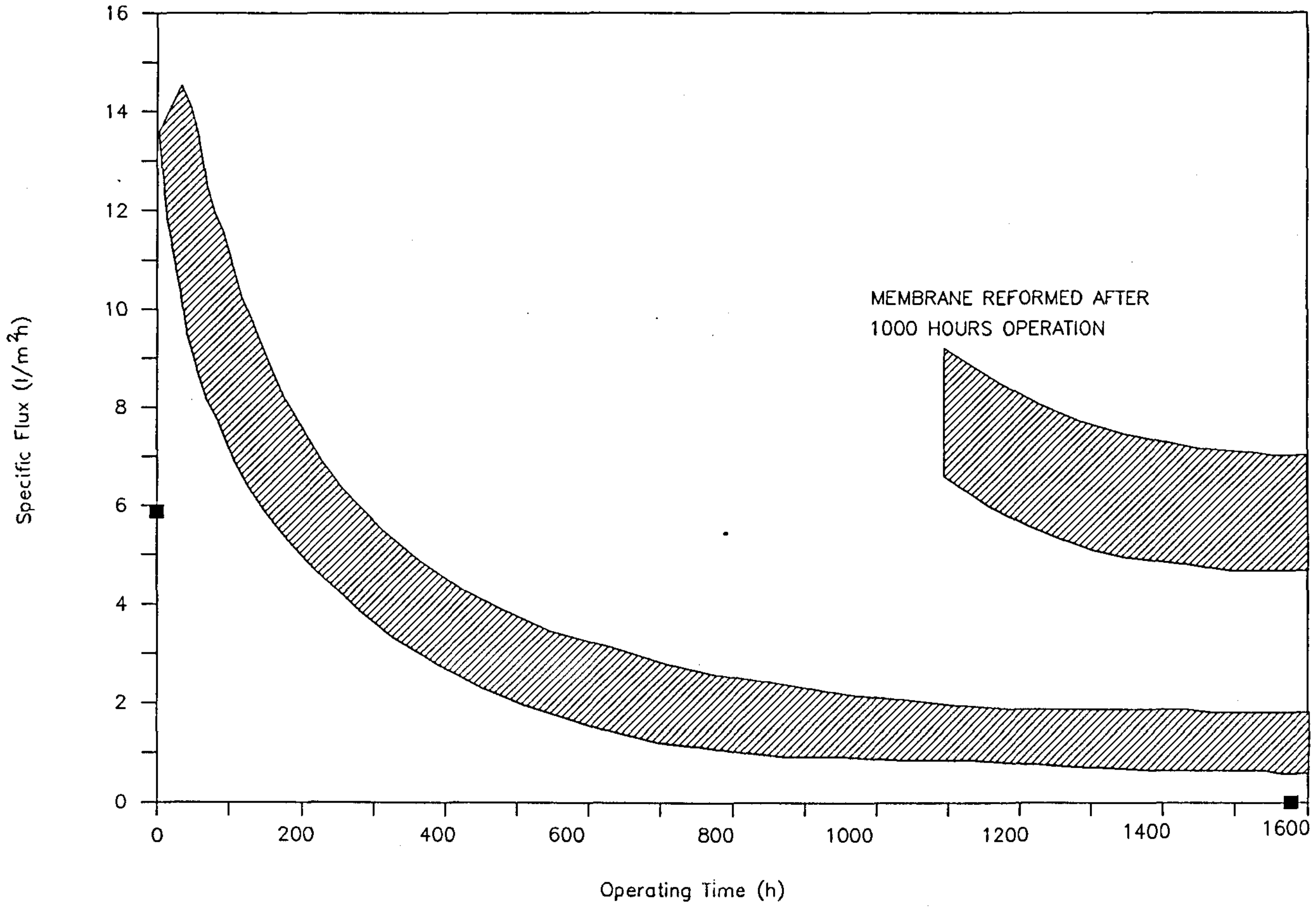


FIGURE 4 : Decline of Specific Flux with Time
Showing Effect of Membrane Reformation

Dynamic membranes have thus been shown to be able to operate under conditions in which conventional membranes have thus far not proved to be succesful.

Because of the possibility of operating under high temperature conditions, there is also the advantage in regard to savings in heat energy which can be a significant factor in deciding on a process route for effluent treatment.

The use of the tubular system used in dynamic membrane separations reduces the potential for physical blockage and thus avoids the need for costly pretreatment.

Acknowledgements

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Subject Index

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2. grease, suint
3. hydrous zirconium (iv) oxide, sintered stainless steel
4. cross-flow, polyacrylic acid
5. ceramic, carbon
6. polyelectrolyte, hydrogen peroxide
7. fouling, flux
8. demonstration plant
12 cleaning, stripping
13. water flux, remembraning

APPENDIX 6

TECHNICAL PERFORMANCE EVALUATION OF THE DYNAMIC MEMBRANE FILTRATION PLANT AT MYM TEXTILES, UMZINTO

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January 1989

SUMMARY

In January 1988, a request was made for an evaluation of the dynamic membrane filtration plant treating textile processing effluent at Mym Textiles, Umzinto. This plant, although originally designed to treat scour effluent, rinse effluent and dye effluent, now treats only a common effluent from the dyeing operations.

Cursory examination shows that microbial growth is not being adequately controlled; rotameters for measuring permeate flow between module banks are virtually unreadable; there are three flow meters on the final permeate lines but only one can be read; the permeate line from Dye 3 stream is piped permanently to sewer.

The flow of effluent to the treatment plant is approximately 300 m^3/d. The evaporator capacity is 50 m^3/d, there is therefore a need to produce about 250 m^3/d permeate. Volume of permeate produced was at the time of assessment, measured to be only about 44 m^3/d. The permeate from some modules was highly coloured. The plant performance based on the volume treated and permeate produced has deteriorated badly over a 40 month period.

It is recommended that :-

(i) As a means of decreasing tube fouling and increasing flux, investigations be undertaken into ways for increasing the low velocity though the tube bundles.

(ii) Dye 2 stream should be closed down and used as an experimental unit for improvements to be made to the whole plant.

(iii) A qualified supervisor should be employed to improve the plant generally and to obtain adequate performance levels using Dye 2 stream initially. The supervisor would be responsible for the day to day operating and monitoring of the plant and also for undertaking tests with a view to continued performance improvement.

The co-operation between Mill Supervision and Effluent Plant Supervision is essential since changes made in the mill, in particular with reference to chemicals used, could easily affect corrosion and performance of the filtration unit. There is little point in making more detailed recommendations on changes or operational methods until agreement is reached regarding overall strategy. However, reference is made in the text to some major changes.

1 INTRODUCTION

In January 1988, Mr. G. Kluk of Mym Textiles requested that the Pollution Research Group of the University of Natal perform a brief technical evaluation of the dynamic membrane filtration plant at their Umzinto Mill. The plant was installed to treat dyehouse effluent with a view to reuse in the dyehouse.

The plant was visited on the 28th January 1988 by Prof. F.G. Neytzell-de Wilde, Messrs K. Treffry-Goatley and M.P.R. Cawdron. During the course of the day, whilst the effluent plant was in its current normal running mode, a comprehensive visual inspection of the plant was performed and a wide range of samples were taken.

Short discussions were held with Messrs van Nieuwberg and Beijer of Mym to assess their opinion of the past, present and future running of the plant.

2 VISUAL INSPECTION

2.1 The Effluent Fed to Filtration Units

The plant was originally designed to operate as three individual units. Each of these units was to treat a specific effluent stream:-

Dye 1 Unit - Scour Effluent
Dye 2 Unit - Rinse Effluent
Dye 3 Unit - Dyeing Effluent

Due to the low permeate production capacity of the plant the effluent treatment strategy was changed and the plant now treats only the dye effluent from the dyehouse. The process effluent from the factory is presently divided into three streams :

(i) Scouring and finishing effluent which is low in colour and dissolved solids. This effluent is discharged direct to sewer.

(ii) Rinse effluent which is low in colour and dissolved solids. This effluent is reused directly in the process.

(iii) Dye effluent which is high in colour with a relatively high ionic content. This effluent is discharged to the membrane treatment plant and the evaporator. It is referred to as the "dirty drain" effluent.

The "dirty drain" flow is approximately 300 m^3/d (from Rapido machines only). Since the evaporator capacity is 50 m^3/d, the total permeate production requirement of the membrane plant should be of the order of 250 m^3/d.

2.2 Storage of Effluent

The effluent is stored in three storage tanks where it is dosed with acid to control pH and also a biocide to control the growth of bacteria. Whilst the pH measured in the plant would seem to indicate adequate pH control, the evidence of "slimy" residues and deposits on the modules and in the plant is indicative of microbial action taking place.

This does not necessarily mean that the wrong biocide is being used but that it is not successfully applied and so is not dealing with the biological problem in the effluent. One possible reason for this is poor mixing of the biocide in the effluent storage tanks.

2.3 The Module Configuration

From the storage tank the effluent is pumped to three Sweco screens to remove the lint. These screens seen to be functioning well and the holes that were evident in the screens on previous visits have been repaired. These three effluent streams are now pumped through heat exchangers into the modules. Each dye stream has its own pump and is operated on a series taper system. The series taper module configuration at present is as follows :-

Dye 1 - 4 : 2 : 2
Dye 2 - 4 : 2 : 1
Dye 3 - 6 : 4 : 2 : 1

There were four modules off line at the time of inspection, two on Dye 2 and two on Dye 3, one of which was being membraned.

2.4 Flow Measurement

There are a number of rotameters on the plant for the purpose of measuring permeate flow between module banks. However, due to a combination of fouling and poor flow through the tubes, the rotameters are virtually unreadable and readings taken from them are at best an estimate. There are three flow meters on the three final permeate lines, only one of which is readable. This is because of the positions in which these meters have been placed. The three meters fo the purpose of measuring reject flow rate would seem to be functioning well.

2.5 Plant Identification

It was observed that there was very little evidence of pipe and/or valve labelling to enable the operator (or visitor) to gain a quick overall picture of the functional aspect of the plant. There would seem to be no standard manual of operation and the current operator, present during the visit, appeared at best to have only a vary basic knowledge of the plant and its function.

2.6 Permeate Fed to Recycle or Sewer

The final permeate from each dye stream is fed to either the recycle tank or the sewer, depending on permeate quality. However, it was noticed that the permeate line from the last bank of modules on Dye 3 stream goes directly to the sewer with no valve installed in the line to allow a choice of permeate flow to the recycle tank. It was felt, at the time of inspection, that the permeate was of an acceptable quality and should have been fed into the recycle tank.

2.7 Corrosion

No shrouds were removed during our inspection and no specific comment regarding corrosion can be made. However, corrosion has been a major problem in the past and we have reason to believe that on removal of the shrouds the corrosion problem will once again be visually evident.

Certainly some modules appeared to be operating poorly due to either leaks from corrosion or faulty membraning.

As has been indicated previously in various reports[1,2,3,4,] the possibility of microbial action (sulphate corrosion) is possible. The presence of chloride in the effluent will also be serious in regard to pitting corrosion especially since foulant materials can be deposited due to the low velocity flow through the tubes and shrouds.

A system where the membrane tubes have been removed from their shrouds and placed in open troughs should be considered. Such a method has been successfully used at an ultrafiltration plant at Uitenhage treating wool scour effluent. It is of interest to note that in correspondence to Mym Textiles from Framatome that this organisation also refers to the tube bundles mounted inside an open stainless steel tank of rectangular shape.

2.8 Low Process Flux Rates

Flux rates are extremely low. Reasons for such low values include :-

(i) a severe foulant in the feed stream,

(ii) low inlet cross-flow velocity in the tubes. It is about 0,5 m/s whereas a higher cross-flow velocity is desirable,

(iii) cleaning procedures are only partly effective. From daily log sheets there is little increase in flux after cleaning.

3 PLANT PERFORMANCE

3.1 The Taper System

One of the main advantages in a series taper stream is the maintenance of a high cross-flow velocity through the system. At the time of inspection a high velocity situation did not exits. It is our opinion that the lack of cross-flow velocity of the fluid through the system generally has been one of the major contributors towards corrosion and fouling.

3.2 Dye 1 System

Dye 1 system was originally used for the scour effluent stream which was the mildest of the three effluent streams. This system is still in the best condition with regard to rejection and permeate flow rate.

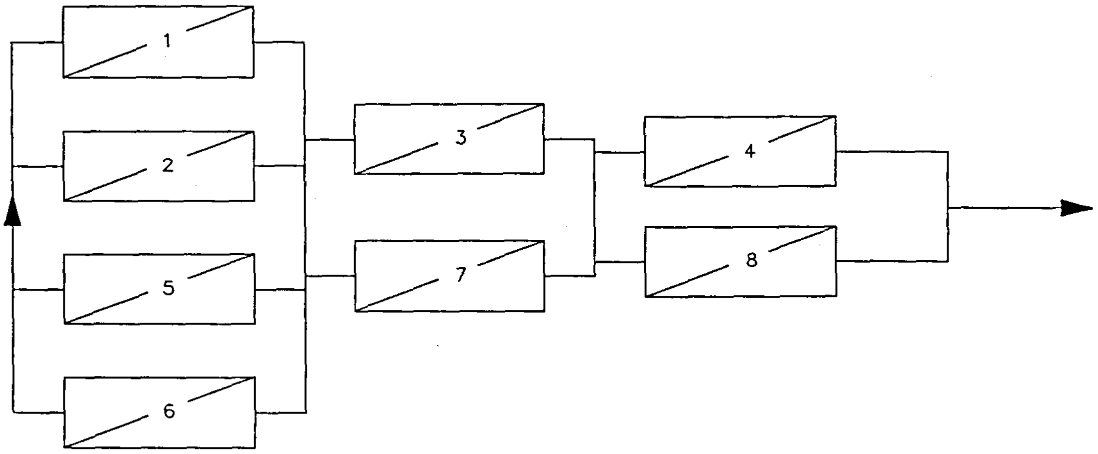
Analysis of the samples taken from Dye 1 system is shown in Table 1.

TABLE 1 : Dye 1 Stream

	pH	Cond (mS/cm)	Chlorides (mg/*l*)	Sulphates (mg/*l*)	Total organic carbon (mg/*l*)	Inorganic carbon (mg/*l*)	Suspended solids (mg/*l*)	Total dissolved solids (mg/*l*)	Colloidal matter (Tyndall Beam)	Detergents
Feed										
before Sweco	7,70	2,32	69	640	346	79	143	1 927	Present	*
at pump	7,70	2,34	76	620	336	59	166	1 994	Present	*
Permeate 1	8,80	0,47	21	100	60	11	-	372	N/D	*
2	8,60	0,43	20	75	60	10	-	435	N/D	*
3	8,80	0,55	31	87	70	11	N/D	601	N/D	*
5	9,10	0,46	20	100	55	11	N/D	445	N/D	*
6	8,60	0,40	22	38	53	8	N/D	347	N/D	*
7	7,40	0,49	28	100	54	12	N/D	428	N/D	*
8	8,20	0,56	32	87	63	13	N/D	425	N/D	*
Reject										
Composite	8,33	3,78	97	990	360	96	346	3 318	Present	*
Permeate										
Composite	7,92	0,52	27	50	50	11	N/D	472	N/D	*

*	=	The methylene blue test indicates that non-ionic surfactants may be present.
N/D	=	Not detected.

Schematically the module configuration is :-



Operating temperature	-	80 °C
Operating pH	-	9,0
Reject flow	-	0,67 m^3/h
*Permeate flow	-	0,74 m^3/h
Feed flow (estimate)	-	1,41 m^3/h
Feed velocity	-	0,56 m/s
Reject velocity	-	0,53 m/s
Inlet pressure	-	5 700 kPa
Outlet pressure	-	5 600 kPa.

*All permeate to recycle.

3.3 Dye 2 System

Dye 2 system was originally used to treat the rinse effluent stream. Dye 2 is in the worst condition of the three units. The possibility exists that at some time in the past a chemical was added during the rinse cycle that was detrimental to the Dye 2 unit.

Analysis of the samples taken from Dye 2 is shown in Table 2.

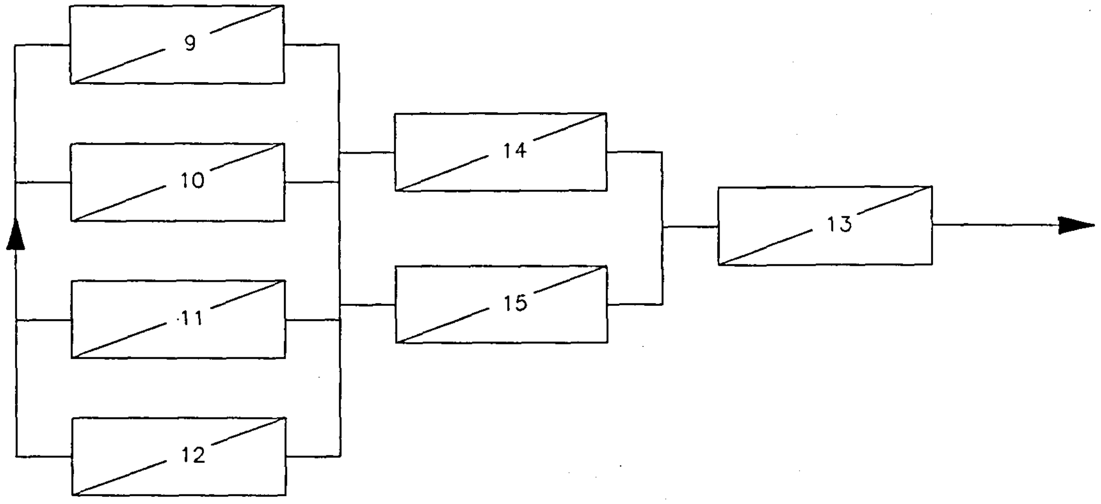
TABLE 2 : Dye 2 Stream

		pH	Cond (mS/cm)	Chlorides (mg/*l*)	Sulphates (mg/*l*)	Total organic carbon (mg/*l*)	Inorganic carbon (mg/*l*)	Suspended solids (mg/*l*)	Total dissolved solids (mg/*l*)	Colloidal matter (Tyndall Beam)	Detergents
Feed											*
before Sweco		7,6	2,22	88	620	431	53	183	2 005	Present	*
at pump		8,0	2,25	89	600	483	23	214	2 070	Present	
Permeate	9	8,3	0,53	30	63	61	14	N/D	263	N/D	*
	10	8,5	1,80	69	520	252	33	112	1 616	Present	*
	11	8,2	0,72	31	100	95	10	38	746	Present	*
	12	8,2	1,15	47	350	165	16	N/D	1 028	Present	*
	13	8,0	0,32	91	550	491	29	N/D	2 302	Present	*
	14	8,6	2,15	86	590	452	33	6	1 998	Present	*
	15	8,4	2,38	91	400	421	29	N/D	2 400	Present	*
Reject											
Composite		8,7	2,67	92	690	397	70	1 438	2 516	Present	*
Permeate											
Composite A		8,8	2,67	86	310	297	29	N/D	2 062	Present	*
Composite B		8,6	1,22	50	225	146	15	N/D	1 054	Present	*

* = The methylene blue test indicates that non-ionic surfactants may be present.

N/D = Not detected.

Schematically the module configuration is :-



(Two modules, not shown above, were not connected into the system).

Operating temperature - 90 °C
Operating pH - 9
Reject flow - 0,6 m^3/h
*Permeate flow - 0,85 m^3/h
Feed flow - 1,45 m^3/h
Feed velocity - 0,57 m/s
Reject velocity - 0,94 m/s
Inlet pressure - 3 800 kPa
Outlet pressure - no pressure gauge.

*Modules 9 to 12 to sewer = 0,257 m^3/h
Modules 13 to 15 to sewer = 0,6 m^3/h
0,85 m^3/h.

3.4 Dye 3 System

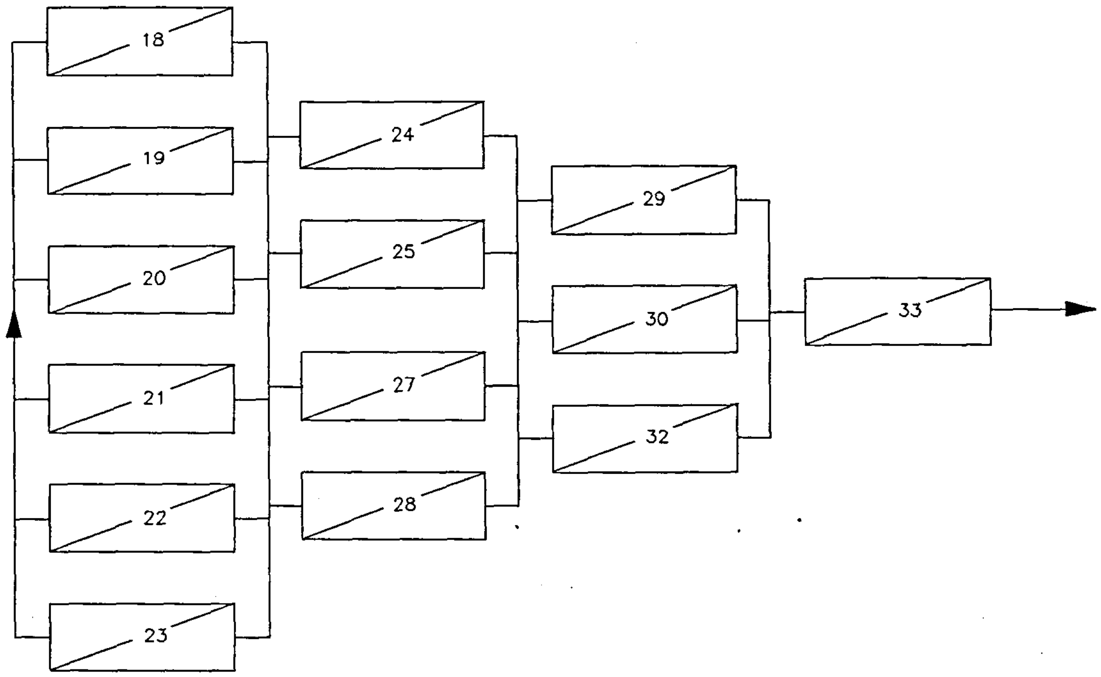
Dye 3 system was originally designed to treat the dye effluent stream which is potentially the worst effluent with regard to fouling. However, as previously mentioned, Dye 3 is given in Table 3.

TABLE 3 : Dye 3 Stream

	pH	Cond (mS/cm)	Chlorides (mg/l)	Sulphates (mg/l)	Total organic carbon (mg/l)	Inorganic carbon (mg/l)	Suspended solids (mg/l)	Total dissolved solids (mg/l)	Colloidal matter (Tyndall Beam)	Detergents
Feed										*
before Sweco	7,9	2,11	82	420	507	44	155	2 075	Present	
at pump	9,0	2,15	90	520	467	14	142	2 117	Present	
Permeate 18	7,5	0,33	18	20	65	10	N/D	326	N/D	*
19	7,8	0,30	16	35	61	10	N/D	308	N/D	*
20	7,5	0,35	22	40	47	8	N/D	107	N/D	*
21	7,6	0,36	24	30	57	4	44	331	Present	*
22	8,8	0,18	53	170	283	7	60	1 082	N/D	*
23	7,7	0,61	33	138	89	7	58	386	Present	*
24	7,8	0,38	26	33	63	8	52	334	N/D	*
25	8,9	0,90	43	40	133	8	30	-	Present	*
27	7,7	0,46	34	75	66	10	N/D	504	Present	*
28	7,2	0,45	29	100	57	14	N/D	482	N/D	*
29	7,3	0,50	39	38	47	19	N/D	414	Present	*
30	7,5	0,61	56	45	58	18	N/D	512	N/D	*
32	9,0	0,54	40	50	57	9	N/D	923	N/D	*
33	8,1	0,77	55	50	65	20	N/D	652	N/D	*
Reject										
Composite	9,5	2,90	122	640	516	29	190	2 730	Present	*
Permeate										
Composite A	9,2	0,67	33	100	95	5	N/D	774	Present	*
Composite B	9,7	0,60	40	50	75	6	N/D	564	Present	*

*	=	The methylene blue test indicates that non-ionic surfactants may be present.
N/D	=	Not detected.

The schematic module configuration of Dye 3 is :-



Operating temperature	-	no reading
Operating pH	-	no reading
Reject flow	-	1,2 m³/h
*Permeate flow	-	0,67 m³/h
Feed flow	-	1,87 m³/h
Feed velocity	-	0,49 m/s
Reject velocity	-	1,89 m/s
Inlet pressure	-	5 600 kPa
Outlet pressure	-	4 600 kPa

*0,343 m³/h to recycle (Comp. A)
<u>0,327</u> m³/h to sewer (Comp. B)
0,67 m³/h

3.5 <u>Performance History</u>

Comparison of the plant during the present inspection and previous inspections is reflected in Tables 4, 5 and 6.

TABLE 4 : Dye 1 System; Performance

	Hours run	Feed	Permeate		Reject
	per day	m³/d	ℓ/m²h	m³/d	m³/d
DESIGN[5]	22	188	78	108	10
Period 8/5/85 - 8/6/85	16	57	47	47	10
Period 27-30/1/86	19	18	7	9	9
28/1/88	19	27	13	14	13

Present observed ionic rejection of Dye 1 system is based on conductivity readings from the composite permeate :-

$$Robs = \frac{(C_f - C_p)}{C_f}$$

Where $C_f = \frac{1}{2}$ (conc. feed + conc. reject)

C_p = conc. permeate.

Therefore Robs = 82%.

TABLE 5 : Dye 2 System; Performance

	Hours run	Feed	Permeate		Reject
	per day	m³/d	ℓ/m²h	m³/d	m³/d
DESIGN[5]	22	298	120	276	22
Period 8/5/85 - 8/6/85	13	74	45	61	13
Period 27-30/1/86	12	65	41	52	13
28/1/88	20	29	17	17	12

Present observed ionic rejection of Dye 2 system based on conductivity readings from the composite permeate.

Robs = 21 %.

TABLE 6 : Dye 3 system; Performance

	Hours run	Feed	Permeate		Reject
	per day	m³/d	ℓ/m²h	m³/d	m³/d
DESIGN[5]	22	198	163	176	22
Period 8/5/85 - 8/6/85	12	61	32	48	13
Period 27-30/1/86	19	85	32	64	21
28/1/88	20	37	7	13	24

Present observed ionic rejection of Dye 3 system based on conductivity readings from the composite permeate.

Robs = 73 %.

The general performance of all three streams show deterioration with particular reference to flows handled.

3.6 Examination of Flux Performance Deterioration

The deterioration of flux values over 40 months operation is given in Table 7.

It is clearly evident from Table 7 that the production rate from the plant has decreased progressively over a 40 month period. This decrease in production rate and the general condition (housekeeping and engineering standard) of the plant and general attitude of personnel to the plant, indicates that it has not been possible for the plant engineer alone to provide sufficient attention to the maintenance and operation of the plant and to general morale and training of operators.

It is considered that the dedicated attention of a supervisor qualified in the technology is necessary.

4 RECOMMENDATIONS

The latest inspection of the plant would seem to indicate that the downhill trend of the plant performance is continuing unabated. To continue running the plant under these conditions is uneconomical in terms of the amount of water recovered. If the current trend continues the plant life span is limited.

Unfortunately over the past few years the plant has suffered some major set-backs and to get the plant back to an economical operating condition the following is proposed :-

(a) Velocity

The cross-flow velocity in the porous tubes of the plant has always been low and this is probably one of the major contributing factors toward the problem of corrosion and fouling. The pumps have a design capacity far in excess of the present feed figures and it is necessary to investigate ways of increasing the plant velocity making use of this spare pump capacity. External corrosion of tubes and internal corrosion of shrouds is likely to be avoided by installing the tube bundles in open troughs. This would eliminate the anoxic conditions which arise in the present system and which encourage corrosion.

TABLE 7 : Output over 40 Months Operation

Date of Assessment	Hours run per day	System No.	No. of modules	Total permeate m^3/d	Average production m^3/module/day
Design :	22	Scour line	9	108	12,0
	22	Rinse line	15	276	18,4
	22	Dye line	18	176	9,8
		Total :	42	560	13,3 (5)
26/3/85	-	Dye 1	9	72	8,0
5 months operation	-	Dye 2	15	76	5,1
	-	Dye 3	18	48	2,7
		Total :	42	196	4,7 (6)
8/5/85 - 8/6/85	16	Dye 1	-	47	-
8 months operation	13	Dye 2	-	61	-
	12	Dye 3	-	48	-
		Total :		156	(7)
27-30/1/86	19	Dye 1	9	9	1,0
15 months operation	12	Dye 2	15	52	3,5
	19	Dye 3	15	64	4,3
		Total :	39	125	3,2 (5)
21/9/87	-	Dye 1	8	26	3,3
35 months operation	-	Dye 2	7	42	6,0
	-	Dye 3	16	57	3,2
		Total :	31	119	3,8 (8)
28/1/88	19	Dye 1	8	14	1,8
40 months operation	20	Dye 2	7	17	2,4
	20	Dye 3	14	13	0,9
		Total :	29	44	1,5 *

* Current report.

(b) **Flux and Rejection**

The general flux figures of the plant are very poor and in some cases the rejection is virtually nil. Fouling and low velocity are likely to be the major reasons for poor flux. Corrosion has caused many leaks in the modules, resulting in poor rejection. At present Dye 2 system is the worst of the three systems, with all its permeate going to sewer. This system should possibly be closed down completely and used as an experimental unit for improvements to be made to the plant in general.

(c) **Qualified Supervision**

To get the plant back to satisfactory condition would, at this stage, require full time supervision by somebody with both a sound chemical background and extensive knowledge of the theory and operation of a dynamic membrane filtration plant. Once the plant is running to specifications this supervision could be reduced to regular inspections of qualified operators. It must be emphasized, at this stage, that it is envisaged that time needed to get the plant back to acceptable performance levels is at least six months with full-time qualified supervision and good workshop co-operation.

(d) **General Plant**

The general state of the plant is poor and the general attitude towards it is negative. Attention to detail is necessary in areas of general plant housekeeping. Flow measurement both in and out of the plant is inadequate, in some cases this may just necessitate the moving and/or cleaning of existing meters and rotameters. The biological problem is still evident and better application of biocide treatment is necessary. A regular record of the chemical performance of the plant is desirable as well as some on-site measuring facilities, such as conductivity meters. Valve markings and clearly visible colour coding of plumbing and equipment would make plant operation easier.

5 GENERAL COMMENT

The condition of the plant necessitates the full time presence of suitably qualified personnel to rectify the situation. This would involve shutting down at least one section of the plant (Dye 2 system) and starting from scratch. The modules need cleaning and in many cases repairing. The cross-flow velocity should be increased and the corrosion aspect re-examined. The removal of the supports from their shrouds and replacing them in open troughs is recommended. This will enable visual inspection and cleaning at any time. This would improve the situation with regard to corrosion and fouling.

The whole operation of the plant from cleaning to membraning and operation should be re-examined and a standard operating procedure drawn up. In the past there seems to have been very little continuity in the running of the plant. Recent technology advances make it advantageous to have more testing done with regard to membraning and membrane compatibility to particular effluents. The selected membrane must also be regularly cleaned to remove the fouling layer to restore flux values.

The co-operation between Mill Supervision and Effluent Treatment Supervision is essential. Changes made in the mill, in particular with reference to the chemicals used, could easily affect corrosion aspects and performance of the filtration unit.

We feel that the potential for the plant to treat the dyehouse effluent still exists but firm action needs to be taken to correct the present situation. This will however, necessitate some capital expenditure.

With regard to the installation of additional modules, we feel that the importance lies in the correction of the faults of the existing modules and their return to proper operating conditions before any consideration is given to extra modules.

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APPENDIX : 7

SHORT TERM PROPOSAL FOR THE IMPROVEMENTS TO BE MADE TO THE ULTRAFILTRATION PLANT AT MYM TEXTILES - UMZINTO

Pollution Research Group
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Durban

January 1989

SHORT TERM PROPOSAL FOR THE IMPROVEMENTS TO BE MADE TO THE ULTRAFILTRATION PLANT AT MYM TEXTILES - UMZINTO

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March 1988

WRC187/88/2/MPC

1 INTRODUCTION

Improvements and modifications are necessary to the ultrafiltration plant. These changes then need to be tested on site under real factory conditions.

At the time of our most recent inspection in February 1988, Dye 2 had seven 7,2 m^2 modules on line and was in the worst condition with regard to colour rejection. We therefore propose that Dye 2 be taken out of commission and used as a pilot plant to model the modifications that are necessary to the plant in general.

2 INSPECTION AND CLEANING

All the modules on Dye 2 need to be thoroughly cleaned and stripped of all foulant and residual membrane material. They must then be removed from their shrouds and inspected for leaks and any evidence of corrosion.

Initially it would be advantageous for two of the more fouled modules on Dye 2 to be removed to the University. This will enable us to inspect the modules with regard to fouling and damage and to assess :

a) The extent of corrosion and leaks and the necessary corrective action to be taken.

b) The extent and nature of the fouling and the best ways to treat the foulant so as to get the sintered tubes back to a bare metal state.

Once these assessments have been made, the cleaning and inspection can continue on site at the Umzinto mill.

3 MEMBRANING

Research carried out at the University of Natal has indicated some advantages of dual layer zirconium/polyacrylic acid membranes as opposed to a straight single layer zirconium membrane. We therefore propose that the two modules at the University be membraned, one with zirconium and the other with zirconium/polyacrylic acid. These modules will then be removed to the Umzinto mill for evaluation on site. Once this investigation has been carried out the membraning procedure and process will be removed to Umzinto and the remaining modules will be membraned utilizing the membraning plant already on site.

4 VELOCITIES

Low cross-flow velocities on the ultrafiltration plant in general have been a cause of concern for some time. These low velocities have probably been one of the causes of corrosion and fouling in the past.

We propose that the problem be approached in two ways :

a) Theoretically

A mathematical model of the modules will be constructed and an in depth analyses of the hydraulics of the flow system will be examined.

b) **Practically**

A thorough inspection of the pump and plumbing systems on Dye 2 will be necessary to investigate ways to obtaine higher flow rates whilst keeping costs down.

5 MODULE CONFIGURATION

The practice of housing the sintered support tubes in shrouds is not suitable. We propose that the supports be removed from the shrouds and laid out in open troughs, preferably constructed of 316 stainless steel. This will help to solve the problem of corrosion within the shrouds and will facilitate regular inspection. This layout has recently been inspected by Messrs Bannister and Beyers at the ultrafiltration plant at the Gubb & Inggs wool scour plant in Uitenhage.

6 LABORATORY SCALE INVESTIGATION

Certain characteristics of the dyehouse effluent need to be examined against the membranes with regard to rejection and flux. We propose that whilst the cleaning and re-membraning programme is proceeding, laboratory scale tests will encompass the performance of both single and dual layer membranes when exposed to dyehouse effluent.

Further investigations will take place to establish an efficient method of cleaning the modules periodically during normal operation. Recent research has shown that an effective method of removing the fouling layer from the tubes, whilst not damaging the membrane, is vital in maintaining good flux levels.

7 DYEHOUSE CO-OPERATION

The successful operation of the ultrafiltration plant is largely dependent on knowledge of the feed effluent. It is therefore important to maintain good communications with the dyehouse with regard to changes in the dyeing process, particularly with regard to the addition of chemicals which will ultimately see the ultrafiltration membranes.

FINAL REPORT

RESEARCH AND DEVELOPMENT OF POLYMEYERS FOR THE FORMATION OF DYNAMIC MEMBRANES AND THE EVALUATION THEREOF FOR THE TREATMENT OF INDUSTRIAL EFFLUENTS

PART 2

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February 1989

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CONCEPT

Dynamically formed membranes are reverse osmosis membranes that are formed in situ by solution chemistry. The membranes comprise a hydrous metal oxide base layer, normally hydrous zirconium (IV) oxide, and a organic polyelectrolyte salt rejecting layer, normally poly(acrylic acid). Research at the Institute for Polymer Science (IPS) at the University of Stellenbosch centered on the developement of alternative polyelectrolytes to supersede poly(acrylic acid).

INTRODUCTION

Research at the IPS on dynamic membranes during the period January 1984 to December 1988 can be divided into two seperate approaches:

1. The initial stage, January 1984 to December 1985, involving the study of:

   (a) substituted acrylic acid homo- co- and terpolymer membranes, and
   (b) maleic anhydride copolymer membranes.

2. The second stage, January 1986 to December 1988, which involved the use of poly(acrylic acid-co-vinyl acetate) and poly(acrylic acid-co-vinyl alcohol) as dynamic membrane polyelectrolytes.

THE PERIOD JANUARY 1984 TO DECEMBER 1985.

The research done at the IPS on dynamic membranes during this period of time is completely described in the masters theses by van Reenen *(1)* and Dowler *(2)*. A compilation of the significant experimental details and results are given below.

BACKGROUND

The research in this initial period was based on the assumption that the salt rejection by these dynamically formed membranes was due solely to the presence of charge on the membrane. Poly(acrylic acid) was, and still is, commercially used. This polyelectrolyte is ionised at neutral pH (see Figure 1), thus giving a membrane that is negatively charged. Based on the available information, it was assumed that if

a) the density of the carboxylic acid groups on the polymer could be increased, and
b) the acid strength of the carboxylic group could be enhanced,

the rejection capability of a membrane could be increased.

RESULTS

Substituted acrylic acid homo- co- and terpolymer membranes

Van Reenen *(1)* synthesized the following homopolymers, primarily substituted acrylic acid polymers.

(i) Poly(methacrylic acid), code PMAA
(ii) Poly(2-chloro acrylic acid), code PClAA
(iii) Poly(itaconic acid), code PIA

He also synthesized the following copolymers.

(iv) Poly(acrylic acid-co-methacrylic acid), code PAA/PMAA
(v) Poly(acrylic acid-co-itaconic acid), code PAA/IA
(vi) Poly(acrylic acid-co-2-chloro acrylic acid), code PAA/ClAA
(vii) Poly(methacrylic acid-co-2-chloro acrylic acid), code PMAA/ClAA
(viii) Poly(acrylic acid-co-vinyl acetate), code PAA/VAC.

He also synthesized the following terpolymer.

(ix) Poly(acrylic acid-co-methacrylic acid-co-2-chloro acrylic acid), code TERP.

The polyelectrolytes were used to form dynamic membranes, as was poly(acrylic acid), for comparative purposes. Details of the polymerization reactions, characterization methods and membrane formation equipment and techniques are fully described in van Reenen's masters thesis *(1)*.

The best membrane results obtained with these polyelectrolytes are given in Table 1.

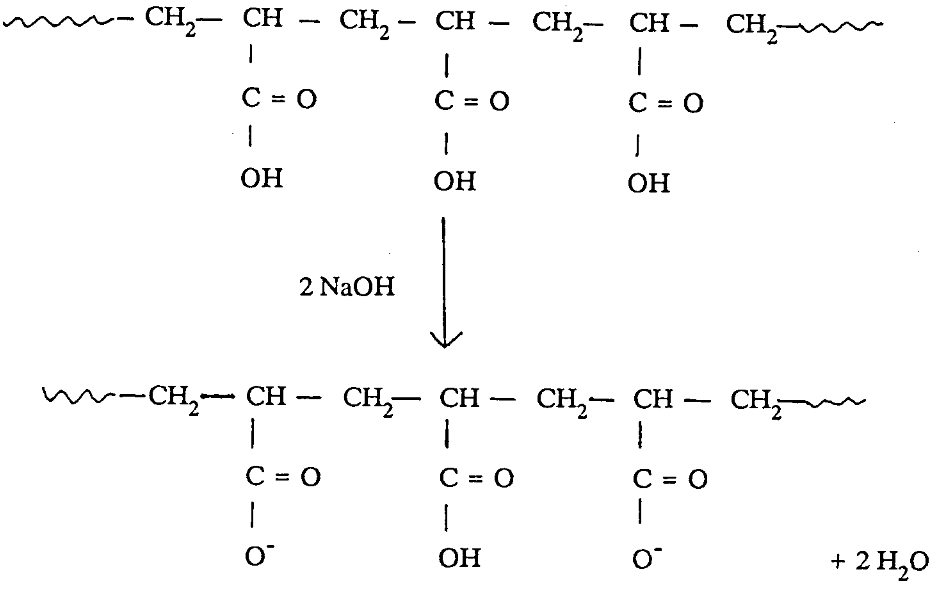

Figure 1. Ionisation of poly(acrylic acid).

TABLE 1: POLYELECTROLYTE CHARACTERISTICS AND MEMBRANE PERFORMANCE DATA.

Polymer code	Composition (Monomer ratio)	Mol. mass	pH 7^1		pH 8		pH 9	
			R	J	R	J	R	J
PAA	-	75 000	90,4	87	93,2	75	90,2	79
PIA	-	43 200	54,7	423	57,8	423	61,0	400
PClAA	-	99 000	60,6	370	64,1	355	65,6	347
PMAA	-	138 000	71,8	408	77,1	348	75,2	355
PAA/MAA	50/50	30 000	Not evaluated as membrane					
PAA/IA	65/35	41 000	78,0	249	81,9	219	85,9	181
PAA/ClAA	60/40	95 200	79,2	344	79,8	332	84,5	302
PMAA/ClAA	50/50	50 000	58,1	521	60,1	498	63,6	460
TERP	40/35/25	63 500	61,7	476	66,8	446	69,2	430
PAA/VAC	-	113 600	93,2	163	95,4	140	93,5	147

R: Rejection of $NaNO_3$ (%).
J: Permeate flux (litre/m^2/hour).
Superscript 1: 24 hours after membrane formation. Subsequent readings (pH) taken at 30 minute intervals after this reading.

As can be seen from Table 1, none of the more highly charged polyelectrolytes show any improvement over poly(acrylic acid) in terms of rejection capabilities, although much higher fluxes are obtained. The only membrane to show any improvement over poly(acrylic acid) is the poly(acrylic acid-co-vinyl acetate) membrane. In this instance the comonomer with acrylic acid is neutral, thus in effect lowering the degree of available ionisable groups. This indicated that the way to increase rejection capabilities of the dynamic membranes was not to increase the charge density, but rather to increase the hydrophobic or neutral content in the membrane.

Maleic anhydride copolymer membranes

Dowler *(2)* synthesized a series of maleic anhydride copolymers. The copolymers were the following:

(i) Poly(maleic anhydride-co-acrylic acid), code MA/AA.
(ii) Poly(maleic anhydride-co-itaconic acid), code MA/IA.
(iii) Poly(maleic anhydride-co-vinyl acetate), code MA/VA.
(iv) Poly(maleic anhydride-co-vinyl alcohol), code MA/VOH.
(v) Poly(maleic anhydride-co-vinyl sulfonic acid), code MA/VSA.

These copolymers were used to form dynamic membranes. Polymerization details and membrane formation techniques are fully described in Dowler's thesis *(2)*. The best results are summarized below (Table2).

TABLE 2: PERFORMANCE OF DYNAMIC ZIRCONIUM OXIDE - MALEIC ANHYDRIDE COPOLYMER MEMBRANES.

Polyelectrolyte	Composition (MA:X)	pH					
		7		8		9	
		R(%)	J(lmh)	R(%)	J(lmh)	R(%)	J(lmh)
PAA*	-	90,0	100	92,3	92	91,0	102
MA/VSA	50:50	58,3	309	61,5	307	62,3	303
MA/IA	50:50	76,7	290	79,3	287	81,4	263
MA/AA	50:50	80,9	211	84,2	198	81,2	208
MA/VOH	50:50	88,2	184	90,3	164	91,1	122
MA/VA	50:50	89,2	100	91,0	87	90,7	81

6000 kPa, 6 m/s, 35°C, 2000 ppm NaNO$_3$, * Poly(acrylic acid)
R : rejection of NaNO$_3$
J : permeate flux
lmh : litres per meter squared per hour

As can be seen from Table 2, all the MA copolymers form dynamic membranes. It is further obvious that the more highly charged copolymers such as MA/IA (2 carboxylic acid groups per monomer unit) and MA/IA (1,5 carboxylic acid groups per monomer unit) exhibit rejection far below that of the PAA membranes (one carboxylic acid group per monomer unit). Increasing the charge density of a dynamically formed polyelectrolyte membrane does not, therefore, increase the rejection of such a membrane. The rejection of the MA/VA and MA/VOH copolymer membranes is introduced is markedly better, though. These results, as with results obtained from the PAA/VAC membranes (see Table 1) indicated that there is a contribution to the salt rejection by dynamically formed polyelectrolyte membranes of the hydrophobic (uncharged) sections of the polyelectrolyte. There were further indications that to increase the hydrophobic content of the copolymers could enhance the rejection. These results led to a change in the research approach for the time period 1986-1988.

THE PERIOD JANUARY 1986 TO MARCH 1988.

Van Reenen *(3)* concentrated in this period of time an the synthesis, characterisation and testing as dynamic membrane polyelectrolytes of a series of poly(acrylic acid-co-vinyl acetate) and poly(acrylic acid-co-vinyl alcohol) copolymers.

The synthesis involved the making of a well-defined range of poly(acrylic acid-co-vinyl acetate) polymers, having different compositions, and the hydrolysis of a range of these copolymers to the resultant range of poly(acrylic acid-co-vinyl alcohol) copolymers of varying compositions. Selected copolymers were also partially hydrolyzed to the resultant poly(acrylic acid-co-vinyl acetate-co-vinyl alcohol) terpolymers.

Characterisation of these copolymers involved composition analysis by means of nuclear magnetic resonance spectroscopy and base titration, water uptake capability or osmotic pressure measurements, and the ability of the copolymers to interact with zirconium in acidic medium. The techniques and apparatus used in the polymerization and characterization are fully described in van Reenen's thesis *(3)*.

RESULTS

The results are divided into three seperate sections.

A. Polymerisation and characterisation.
B. Membrane results.
C. Results pendant to and arising from the original study.

A. Polymerisation and characterisation

Polymerisation. The polymerisation techniques are given in full in van Reenen's thesis *(3)*. The table with polymerisation mixtures as well as polymer codes are given below (Table 3). Selected AVAC copolymers were hydrolyzed fully to give the poly(acrylic acid-co-vinyl alcohol) copolymers, codenamed AVOH. The numerical extension of the mother polymer code remained the same. For example, AVAC 2a would be hydrolyzed to AVOH 2a, AVAC 17 to AVOH 17 *etc.*

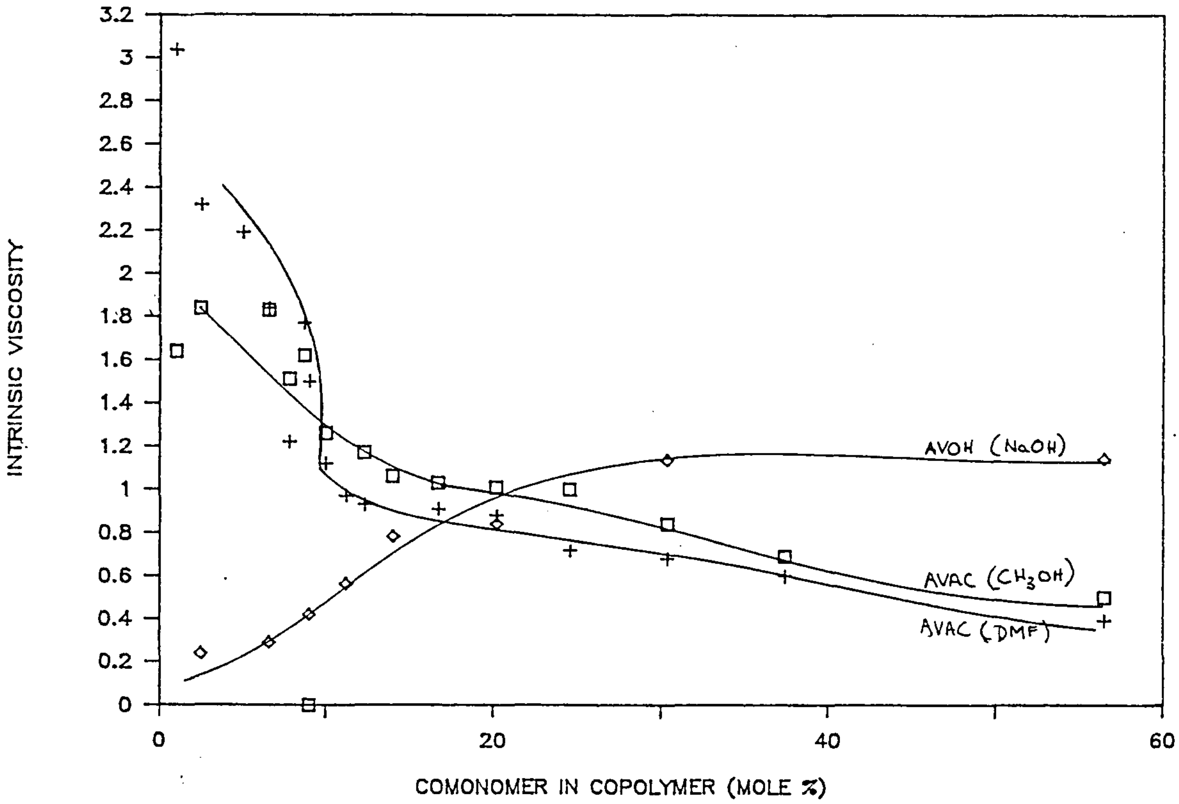

Figure 2. Intrinsic viscosities of co- and terpolymers.

TABLE 3: THE REACTION MIXTURES FOR POLY(ACRYLIC ACID-CO-VINYL ACETATE) COPOLYMERS.

Polymer Code	Acrylic acid		Vinyl acetate		1,4-Dioxane	Bz_2O_2	
	g (x10)	moles ($x10^{-1}$)	g (x10)	moles ($x10^{-1}$)	m*l* ($x10^2$)	g (x10)	moles ($x10^{-3}$)
AVAC 1	6,90	9,58	0,50	0,58	1,50	3,00	1,24
AVAC 2	6,48	9,00	0,89	1,03	1,50	3,00	1,24
AVAC 2a	6,44	8,94	0,88	1,03	1,50	5,31	2,19
AVAC 2b	6,54	9,08	0,94	1,09	1,50	3,03	1,25
AVAC 2c	6,42	8,92	0,90	1,05	1,50	3,02	1,25
AVAC 3	6,10	8,47	1,40	1,63	1,50	3,06	1,26
AVAC 4	5,80	8,05	1,70	1,98	1,50	3,00	1,24
AVAC 4a	5,80	8,05	1,69	1,97	1,50	5,43	2,24
AVAC 4b	5,87	8,15	1,69	1,97	1,50	2,99	1,23
AVAC 4c	5,83	8,10	1,72	2,00	1,50	2,98	1,23
AVAC 5	5,40	7,50	2,10	2,44	1,50	3,10	1,28
AVAC 6	5,02	6,97	2,48	2,88	1,50	3,06	1,26
AVAC 6a	5,02	6,97	2,46	2,86	1,50	1,52	0,63
AVAC 6b	5,02	6,97	2,48	2,88	1,50	4,82	1,99
AVAC 7	4,50	6,25	3,00	3,49	1,50	3,10	1,28
AVAC 7a	4,90	6,24	2,95	3,43	1,50	1,57	0,65
AVAC 7b	4,53	6,29	2,95	3,43	1,50	3,01	1,24
AVAC 7c	4,50	6,25	2,99	3,48	1,50	3,04	1,26
AVAC 8	4,00	5,55	3,91	4,55	1,50	3,12	1,29
AVAC 8a	4,00	5,55	3,88	4,51	1,50	3,09	1,28
AVAC 8b	4,10	5,69	4,09	4,76	1,50	3,85	1,59
AVAC 9	3,61	5,01	4,26	4,95	1,50	3,00	1,24
AVAC 9a	3,62	5,03	4,25	4,94	1,50	3,00	1,24
AVAC 9b	3,68	5,11	4,36	5,07	1,50	3,10	1,28
AVAC 10	3,26	4,53	4,73	5,50	1,50	3,11	1,28
AVAC 10a	3,27	4,54	4,70	5,47	1,50	3,01	1,24
AVAC 11	2,84	3,94	5,17	6,01	1,50	3,03	1,25
AVAC 12	2,53	3,52	5,62	6,54	1,50	2,95	1,22
AVAC 12a	2,58	3,58	5,67	6,59	1,50	3,06	1,26
AVAC 12b	2,47	3,43	5,78	6,72	1,50	3,09	1,28
AVAC 13	2,17	3,01	6,01	7,06	1,50	3,01	1,24
AVAC 13a	2,13	2,96	6,08	7,07	1,50	3,00	1,24
AVAC 14	1,87	2,59	6,42	7,47	1,50	3,04	1,26
AVAC 15	1,44	2,00	6,90	8,02	1,50	2,98	1,23
AVAC 15a	1,45	2,01	6,97	8,10	1,50	2,56	1,06
AVAC 15b	1,47	2,04	6,84	7,95	1,50	2,98	1,23
AVAC 15c	1,49	2,07	6,82	7,93	1,50	3,07	1,27
AVAC 16	1,08	1,49	7,22	8,52	1,50	3,15	1,30
AVAC 16a	1,01	1,40	7,85	9,13	1,50	2,02	0,84
AVAC 17	0,37	0,51	8,24	9,58	1,50	3,08	1,27
AVAC 17a	0,39	0,54	8,18	9,51	1,50	1,51	0,62
AVAC 17b	0,39	0,54	8,14	9,47	1,50	3,04	1,26

Molecular mass. Only a few polymers in the AVAC range of copolymers were soluble in the the only suitable eluent to use in gel permeation chromatography (GPC), THF. The molecular masses obtained with GPC are given in Table 4. It can safely be assumed that the molecular masses of the other polymers would be similar as the reaction temperature and initiator concentrations were kept constant in all the reactions, even though the reaction mixture composition was varied. Temperature and initiator concentration are the deciding factors when it comes to the determination of molecular mass of a polymer.

TABLE 4: MOLECULAR MASS AND POLYDISPERSITIES OF AVAC COPOLYMERS DETERMINED BY GPC USING THF AS ELUENT

Polymer	Molecular Mass	Polydispersity
AVAC-15	96 300	2,48
AVAC-14	110 600	2,67
AVAC-13	109 300	2,61
AVAC-12	101 900	3,03
AVAC-11	110 600	3,68
AVAC-10	115 600	2,29
AVAC-09	107 200	-

From the above table it is clear that the molecular masses of the whole range of AVAC polyelectrolytes that were evaluated by GPC are reasonably similar, that is in the region 95 000 to 115 000.

Intrinsic viscosity. The intrinsic viscosities of the AVAC range of copolymers were determined in methanol and N, N,-dimethyl formamide (DMF) respectively, while the intrinsic viscosities of the AVOH range of copolymers were determined in 2 mole.dm^{-3} NaOH. Results are shown in Figure 2.

The intrinsic viscosities of the AVAC copolymers decrease as the vinyl acetate content increases, in both a non-polar solvent (DMF) and a polar solvent (methanol). The intrinsic viscosities of the AVOH polymers increase as the comonomer content increases. These trends show an interesting correlation with the water uptake capability of the copolymers.

Composition analysis. This was done by NMR and titration. A typical NMR scan is shown in Figure 3. The composition analysis is given in Table 5, and the relationship between the amount of vinyl acetate in the reaction mixture and the amount in the polymer is shown in Figure 4.

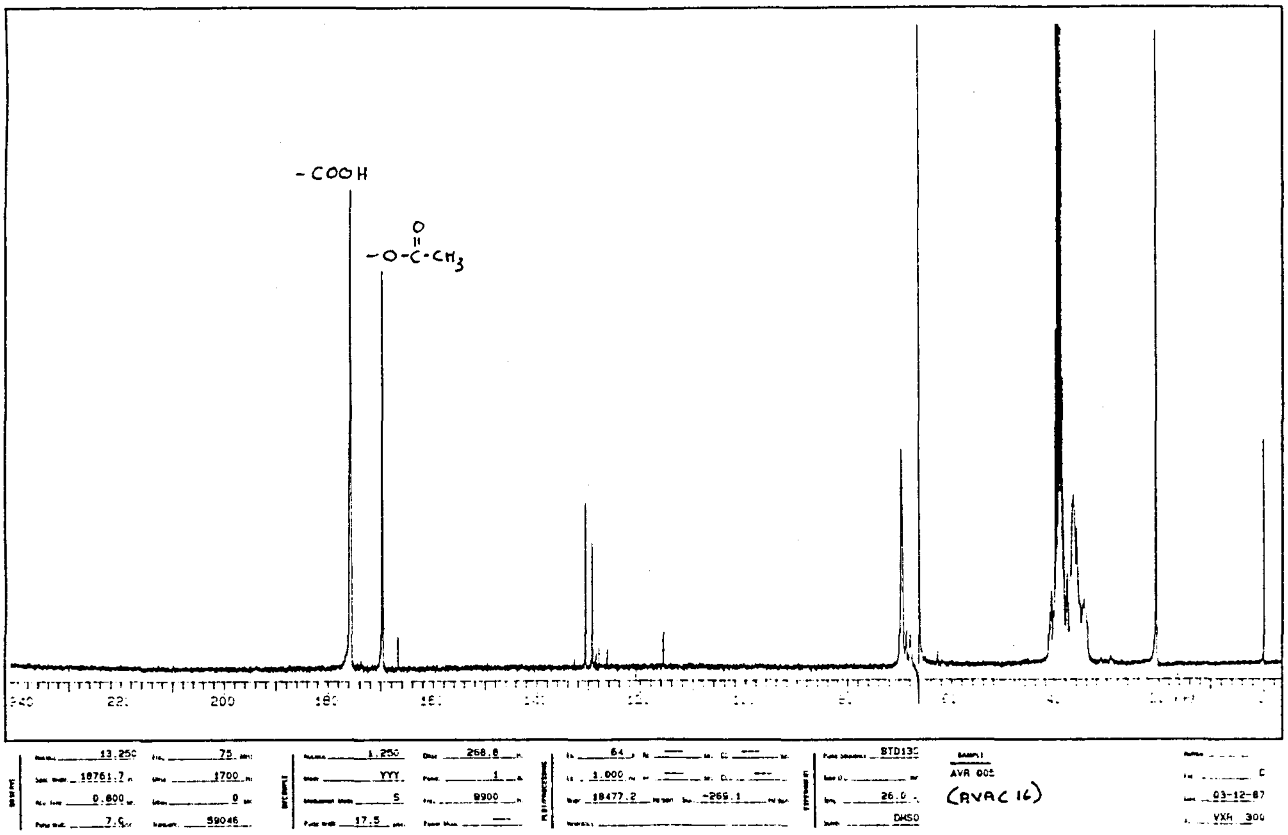

Figure 3. NMR scan of AVAC.16 .

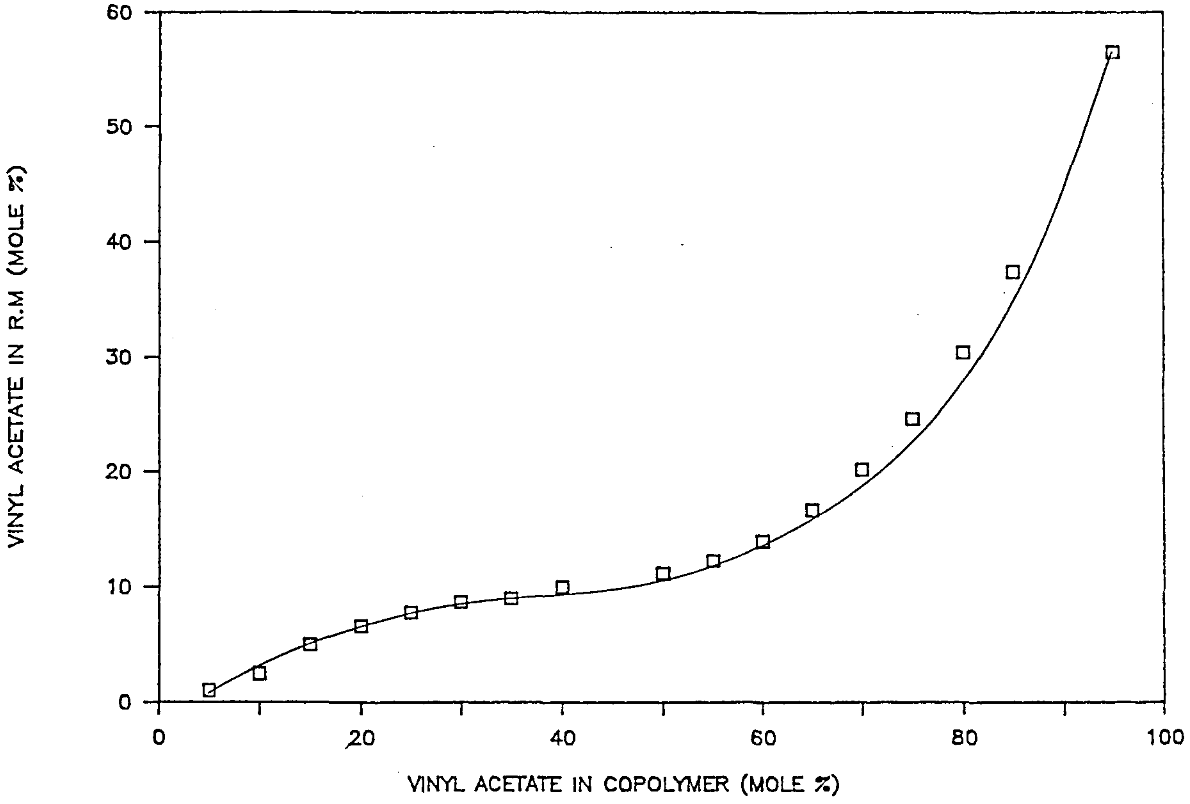

Figure 4. Relationship between vinyl acetate concentration in the reaction mixture and the copolymer composition.

TABLE 5: COPOLYMER COMPOSITION ANALYSIS

	Percentage of vinyl acetate in the polymer		
Polymer	NMR	Base Titration	Acid Titration
AVAC-1	-	1,0	20,0
AVAC-2	3,10	2,5	18,7
AVAC-3	-	5,0	32,3
AVAC-4	4,20	6,6	36,0
AVAC-5	-	7,8	28,4
AVAC-6	-	8,7	24,7
AVAC-7	6,80	9,0	26,8
AVAC-8	-	10,0	26,3
AVAC-9	12,20	11,2	25,8
AVAC-10	-	12,3	34,0
AVAC-11	16,10	14,0	33,0
AVAC-12	-	16,7	28,4
AVAC-13	20,40	20,2	-
AVAC-14	-	24,6	33,8
AVAC-15	-	30,4	39,6
AVAC-16	33,10	37,4	40,5
AVAC-17	56,80	56,5	39,1

Zirconium chelating capability. The technique used was based on the one developed by Simpson *et al (4)*. Results are quoted in Figures 5 and 6. Figure 5 shows the decrease in zirconium uptake capability as the acrylic acid content of the copolymers decrease, and show that the AVOH copolymers are more capable of chelating zirconium, than are the AVAC copolymers. This was to be expected as the hydroxyl group on the AVOH copolymers afford more chance of chelation than does the acetate group on the AVAC copolymers. This point is proved by the results in Figure 6, which shows that with increasing degree of hydrolysis for a given polymer, the degree of interaction with zirconium increases (as measured by the technique used).

Water uptake capability. This measurement is a means of determining the osmotic pressure of these polyelectrolytes, a factor which plays a significant role in polymer membrane performance. Results are shown in Figure 7. Interesting here is the fact that as the acrylic acid content decreases, the water uptake capability of the AVAC copolymers decrease, but the water uptake capapbility of the AVOH copolymers increase as the acrylic acid content decreases. The latter is due to the presence of hydrophylic (water-loving) hydroxyl groups.

B. Membrane results

Membrane peak performance. The results were calculated as the average of the four best sets of membranes. The rejection figures are shown in Figure 8, and the flux results in Figure 9. In Figure 10 the relationship between water uptake capability and flux (AVAC membranes) is shown.

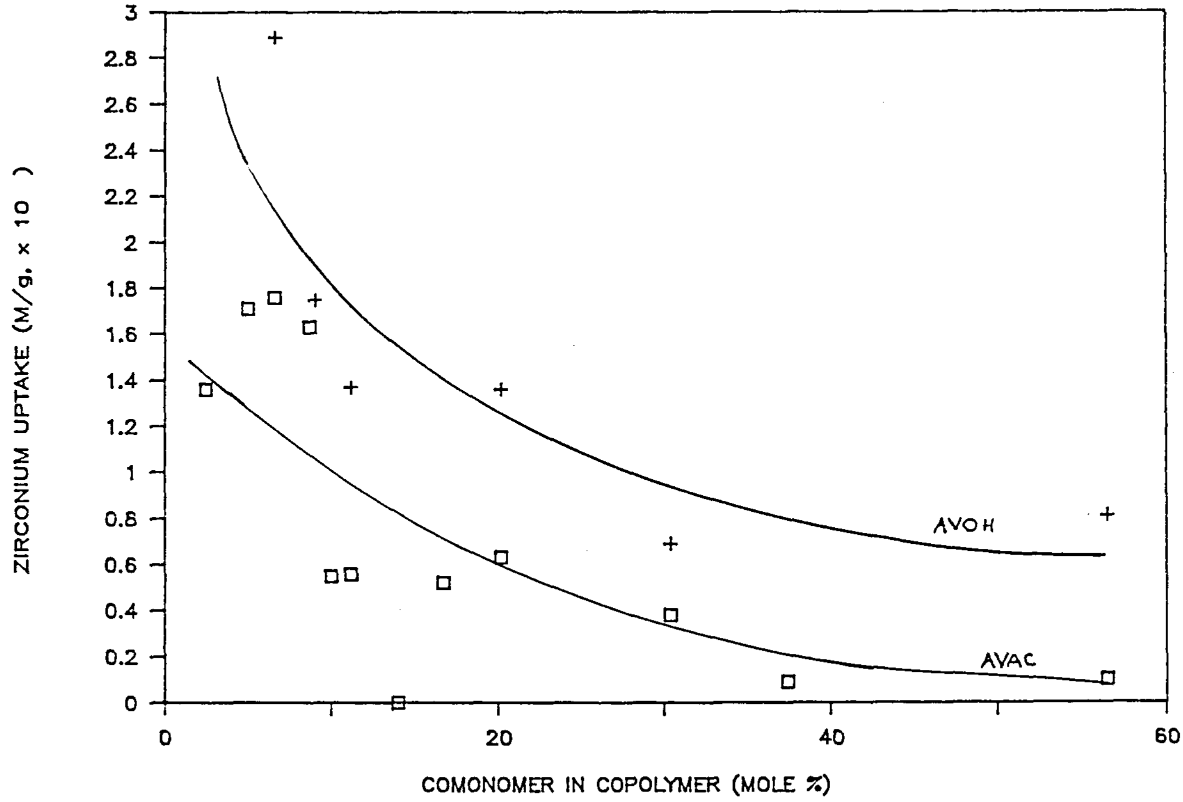

Figure 5. Zirconium chelating capability of the copolymers.

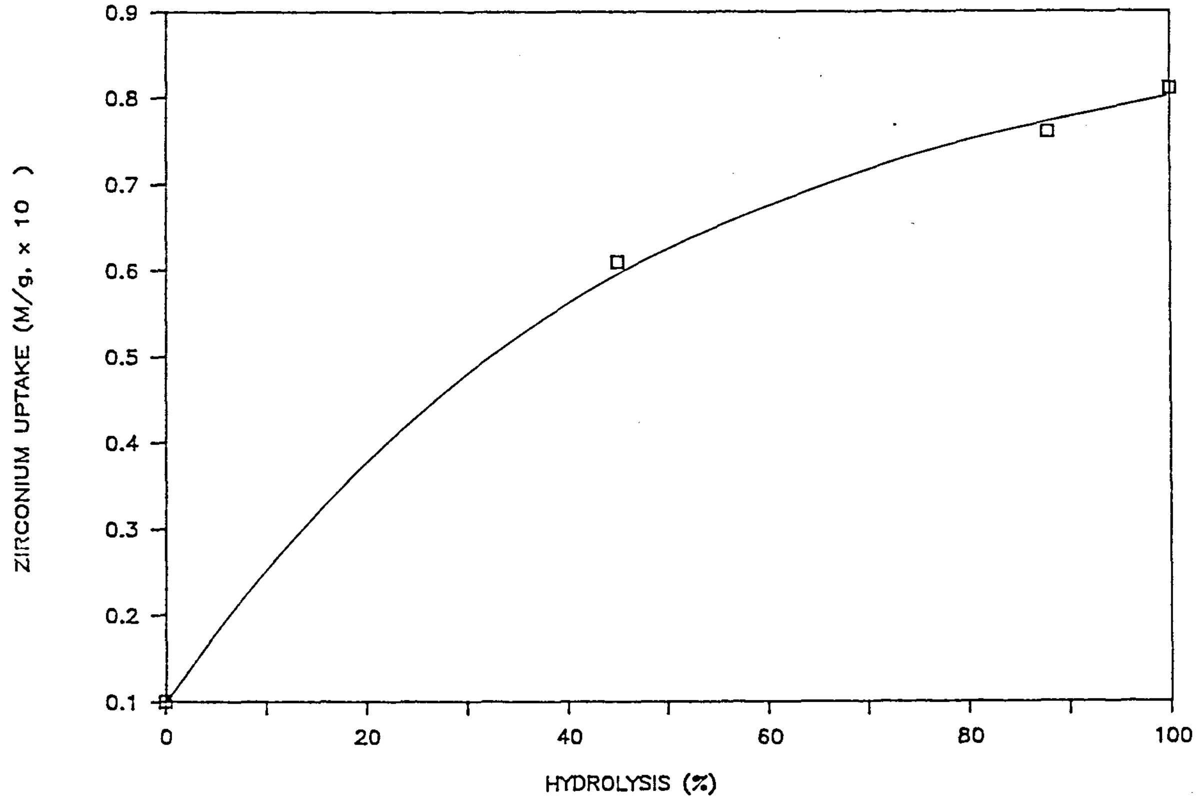

Figure 6. Zirconium chelating capability as a function of the degree of hydrolysis.

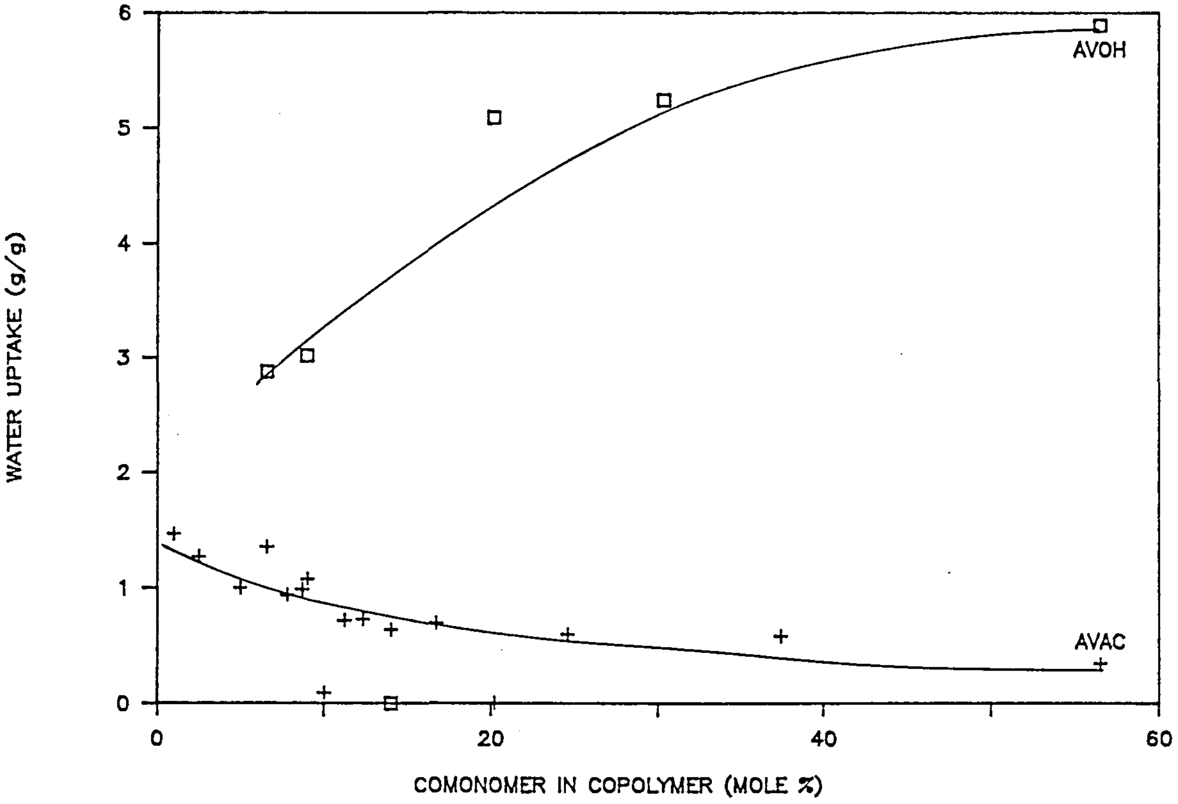

Figure 7. Water uptake capability.

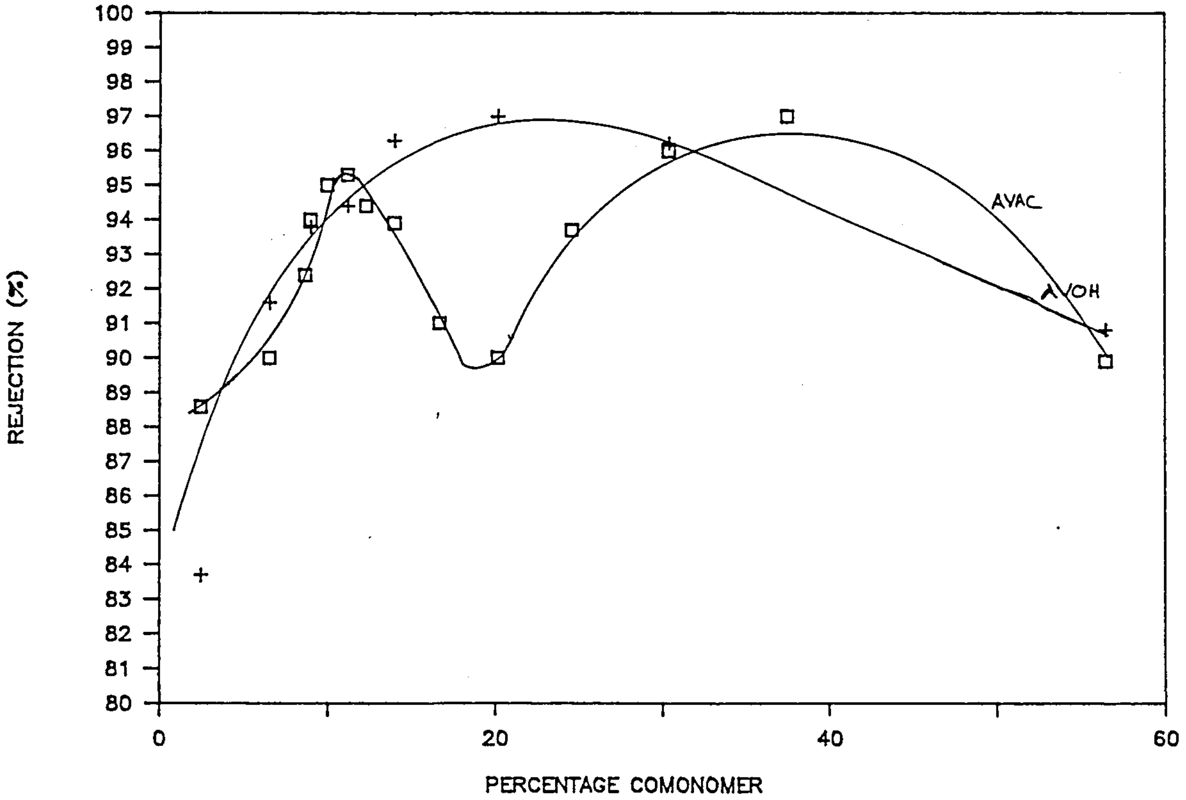

Figure 8. Peak rejection figures.

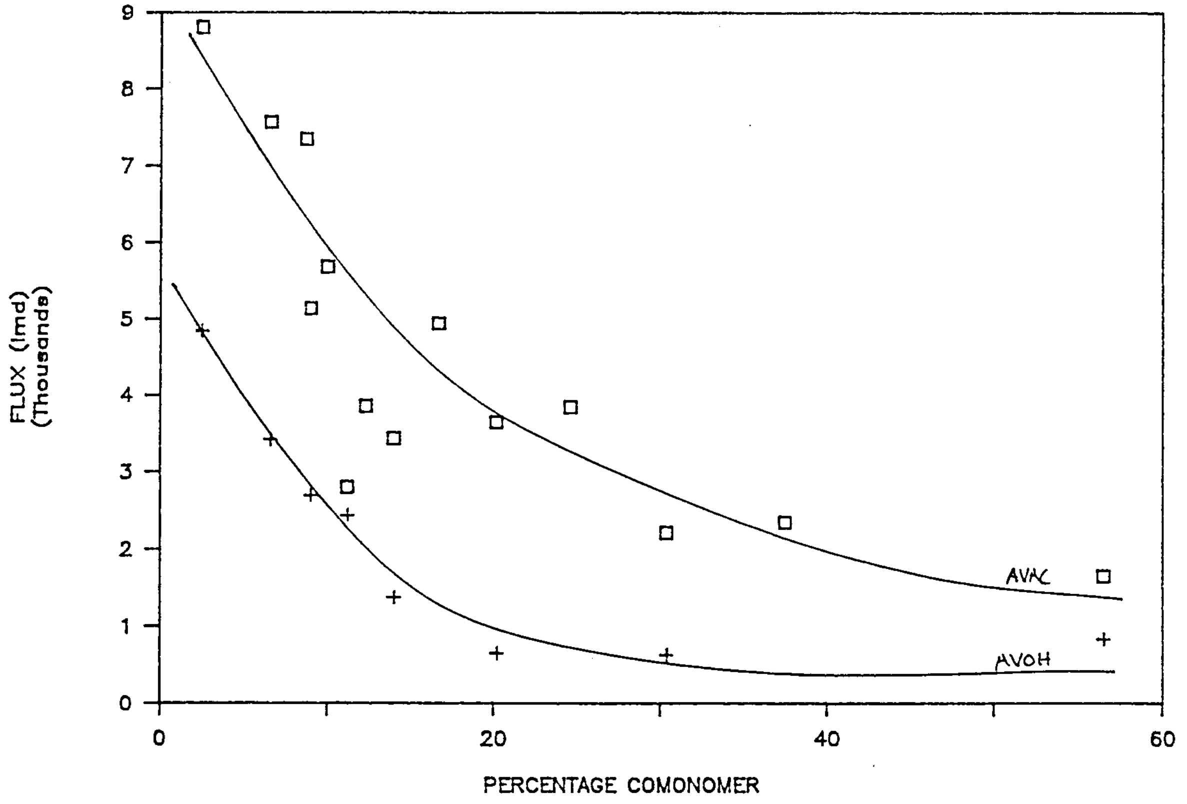

Figure 9. Peak flux figures.

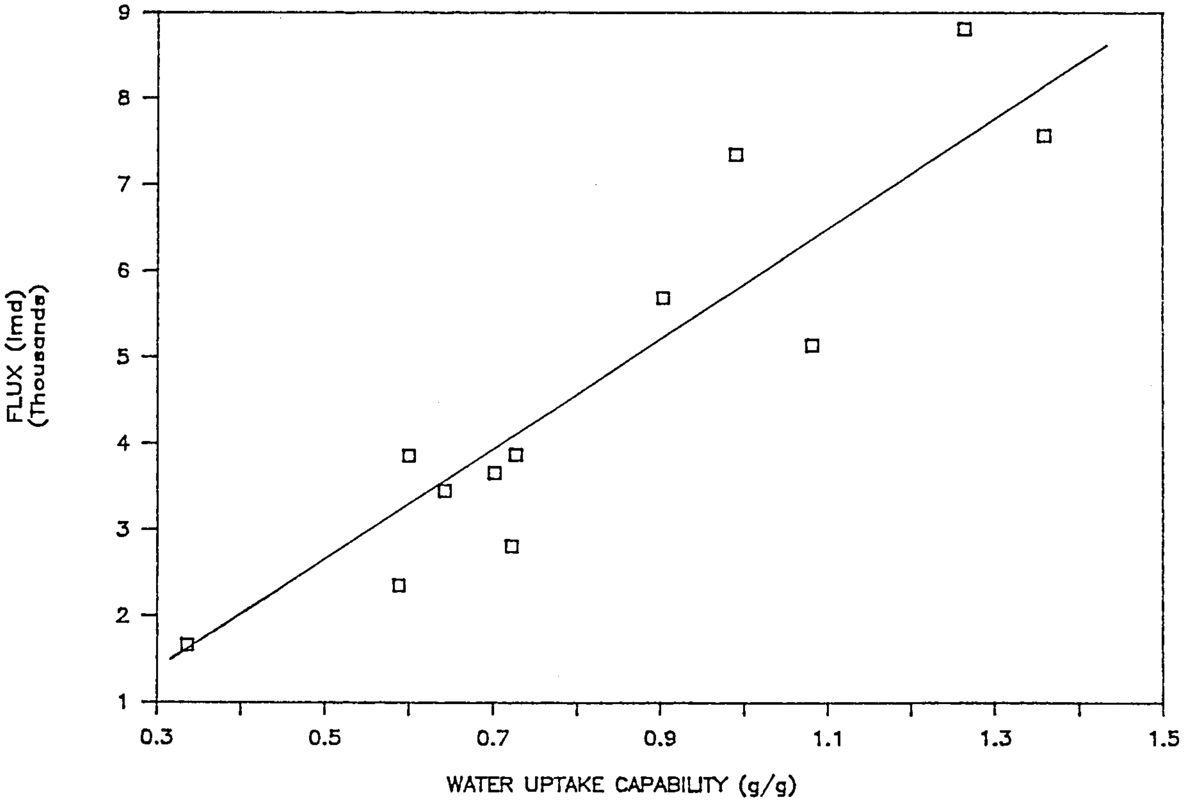

Figure 10. Relationship between water uptake capability and flux, AVAC membranes.

The AVAC copolymer membranes exhibited two rejection maxima, and the AVOH copolymer membranes a single maximum, over the range of copolymers evaluated as dynamic membrane polyelectrolytes.

The best rejection obtained with each of the types of copolymers is of a comparable magnitude, within the ranges of homogeneous copolymer membranes. In the homogeneous range of membranes, the best rejection obtained with the AVAC membranes is 97% (AVAC 16), and the best obtained with AVOH membranes also 97%, (AVOH 13). There is a possibility that the rejections obtained with AVAC 16 and AVOH 13 could be increased by optimisation of membrane formation conditions and polymer molecular mass. These membranes should be investigated further with the express purpose of optimising performance.

The flux obtained at the peak rejection figures for AVAC 16 and AVOH 13 was 2,60 m*l*/min and 0,71 m*l*/min, respectively. The flux decline with changing copolymer composition is shown in Figure 9. Of interest here is the fact that the flux of the AVOH membranes are consistently lower than that of the corresponding AVAC membranes. The flux decline with changing copolymer composition indicate that the flux is primarily influenced by the carboxylic acid content of the membranes. If this is the case, one could expect a given AVAC membrane and the corresponding AVOH membrane to have similar fluxes. Obviously they do not. It is felt that the phenomenon of the lower flux of the AVOH copolymer membranes could best be explained in terms of the water uptake capability and viscosity of the polyelectrolytes. Composite dynamic membranes are formed by a pore-filling mechanism. Thus a polyelectrolyte in a given pore volume will fill a percentage of that pore volume, and that percentage will be determined by the polyelectrolyte viscosity, which in turn will be determined by the water uptake capability. Water in a swollen polyelectrolyte molecule is restricted in its mobility, and the larger this restriction the lower the flux. This argument holds for both the AVAC and AVOH ranges of copolymer membranes, as well as for comparing the two copolymer membrane ranges.

Membrane stability. Stability was determined by the rejection changes in the membrane in the period 24 hours to 48 hours after formation. Stability was expressed as R_{48}/R_{24}, R_{24} being the rejection 24 hours after formation and R_{48} being the rejection after 48 hours. The first 24 hours were regarded as a stabilising period. The results are shown in Figure 11. Of interest here is the fact that the AVOH copolymer membranes are, by and large, more stable than the AVAC copolymers. The reason must be that the presence of the alcohol groups afford a possibility for chelation with the hydrous zirconium oxide, while the acetate groups do not. This was reflected in the results obtained with the zirconium uptake experiments. (See Figures 5 and 6)

The effect of pH. Changes in rejection and flux with pH was determined in terms of two paramaters, R" and J". These are defined as follows:

If R_i and J_i are the rejection and flux values respectively at pH = i, and R_7 and J_7 are the corresponding values at pH 7, then let

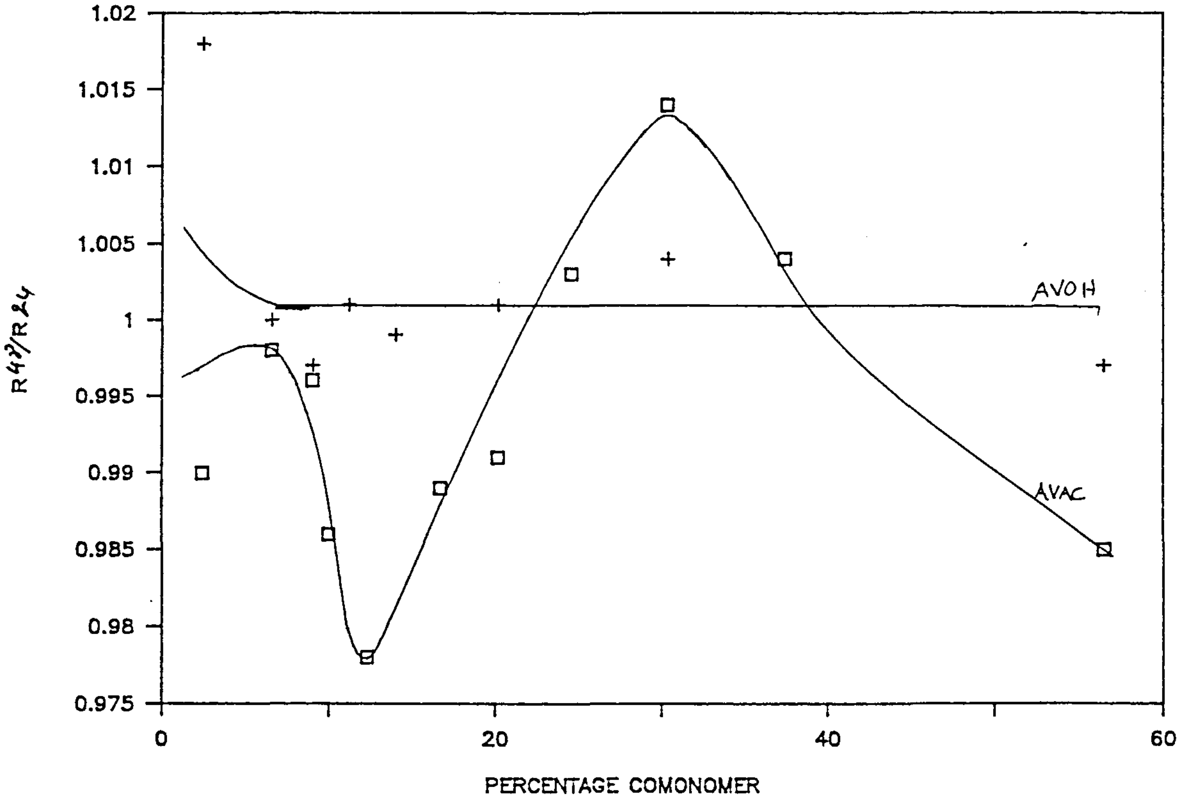

Figure 11. Membrane stability.

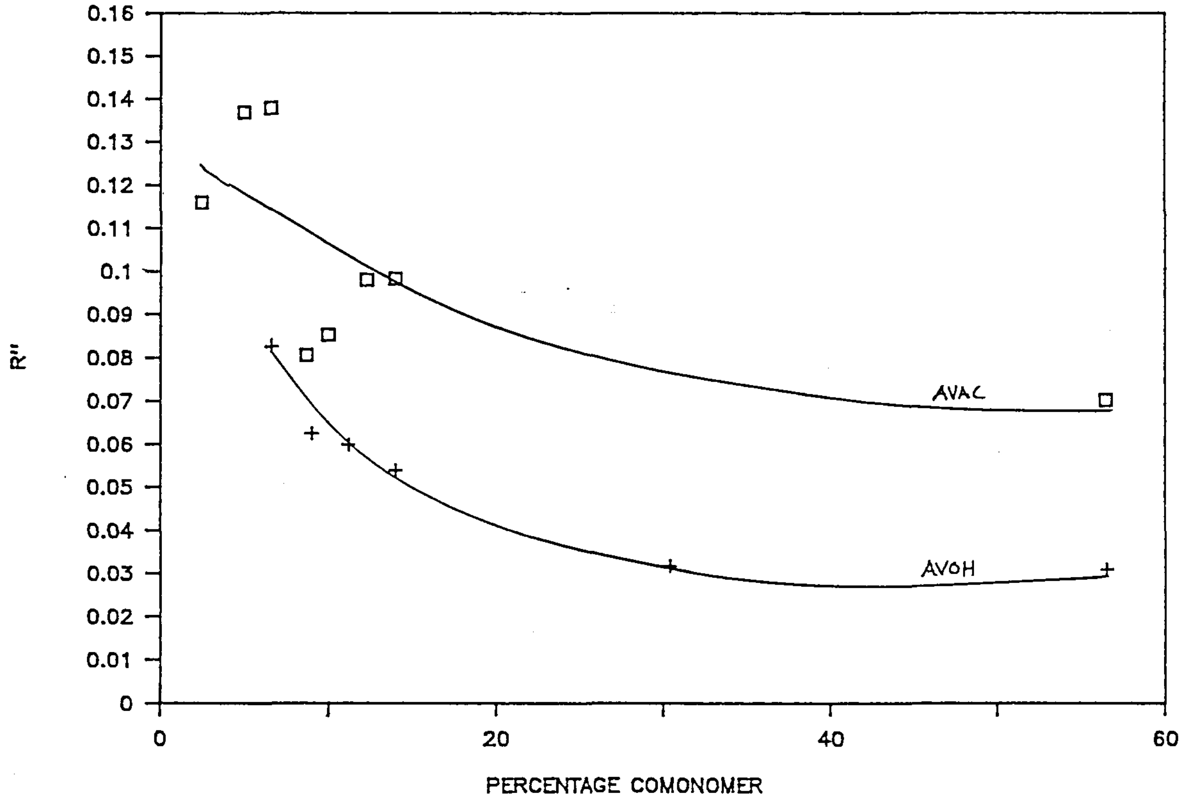

Figure 12. The effect of pH.

$$R = R_i/R_7 \text{ and } J = J_i/J_7 \text{ and let}$$
$$R' = 1 - R; \quad R'' = R'/(7\text{-}i)$$
$$J' = 1 - J; \quad J'' = J'/(7\text{-}i)$$

Using the above equations, the changes in the rejection and flux were calculated as a function of the change in pH. The results are shown in Figure 12. The general effect for both the AVAC and AVOH copolymer membranes is that the pH sensitivity, expressed in terms of R" and J", decreases as the comonomer content in the acrylic acid copolymer membranes increases. There is therefore no difference in the pH sensitivity between the two different types of membranes, in terms of the copolymer composition.

The effect of pressure.

Rejection

The change in rejection sensitivity to pressure in terms of copolymer composition is shown in Figure 13. Here it is noticable that the AVOH copolymer membranes become more sensitive to a change in pressure as the acrylic acid content increases, in contrast with the AVAC copolymer membranes, where the opposite applies. The rejection sensitivity to pressure is dependent on the hydrophilicity of the membranes.

Membrane permeability

The results are given in Figure 14. Of note is that there is a correlation for both types of membranes between the change in membrane permeability and the membrane copolymer composition. In broad terms, the membrane permeability change with changing pressure becomes less for the AVAC copolymer membranes the higher the acrylic acid content is, while the reverse applies for the AVOH copolymer membranes. This is due to the effect that the membrane osmotic pressure has on the effective pressure. The higher the membrane osmotic pressure, the higher the effective pressure the membrane experiences. Thus, the flux decline for a highly hydrophilic membrane will be less than for a less hydrophilic membrane, when the applied pressure is decreased. This trend is consistent for both types of membrane.

The effect of feed concentration.

The effect of feed concentration on the rejection

The result of a changing feed concentration on the observed rejection of the membrane is given in terms of the slope of the log (solute flux) (log (1 - R)) *versus* log (feed concentration) (log M) plots. The results are shown in Figure 15. These results are an anomaly. The slope of the above relationship decreases for an increasing comonomer content in the AVAC copolymer membranes, as were to be expected. For the AVOH copolymer membranes, however, the slope remains reasonably constant as the membranes become more neutral. This is anomalous, especially as the flux sensitivity to feed concentration decreases for increasingly neutral membranes, indicating decreasing charge density. The slope should, therefore, decrease as the

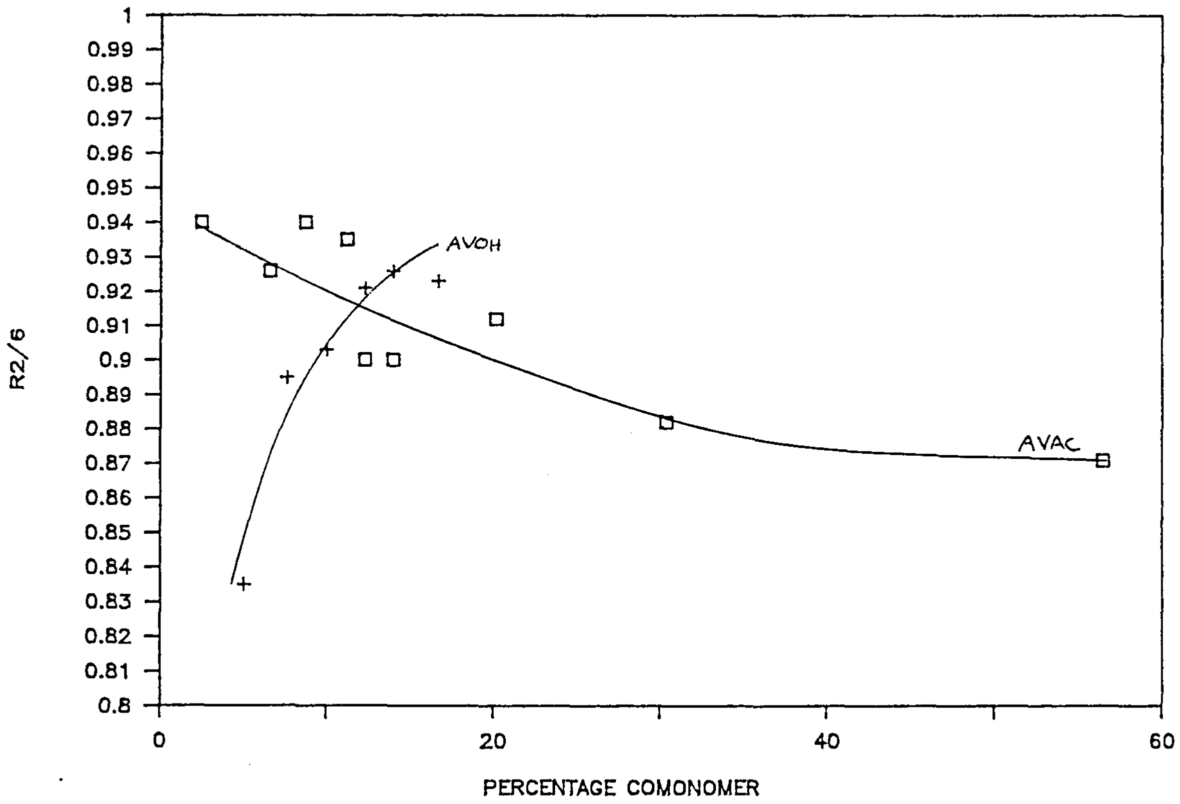

Figure 13. The effect of pressure on rejection.

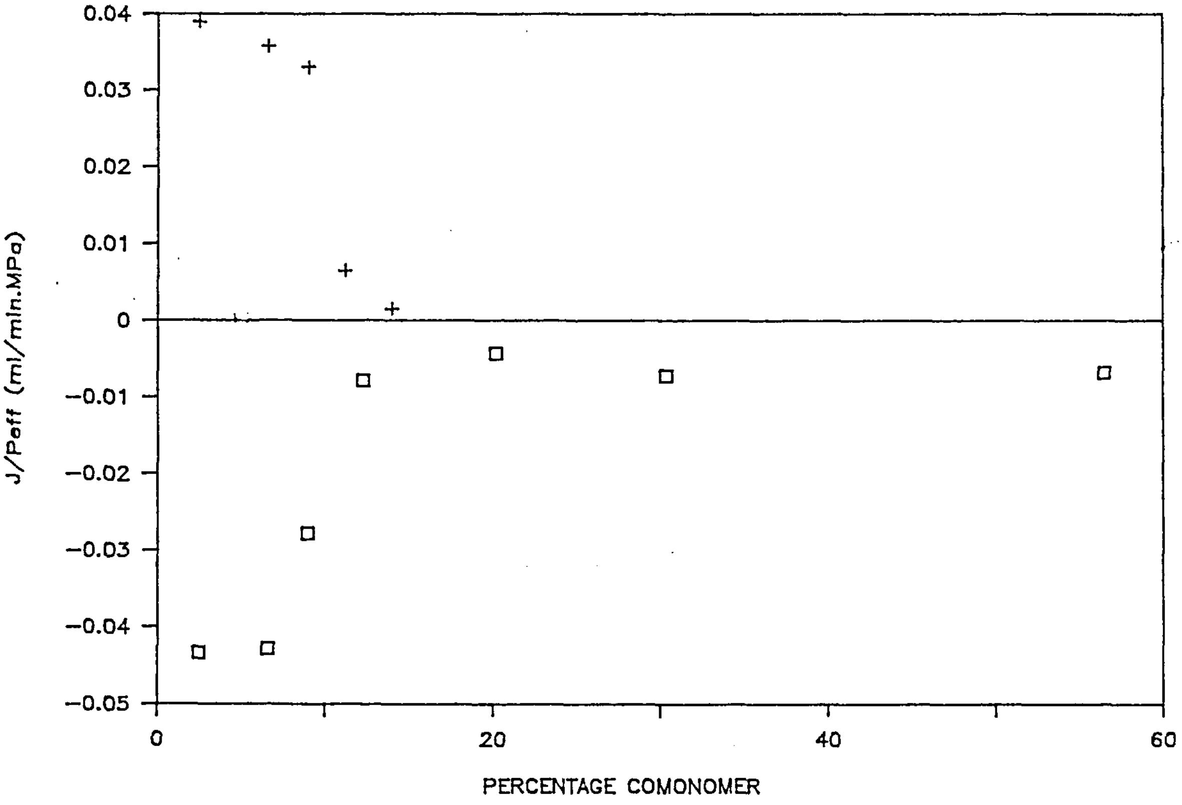

Figure 14. The effect of copolymer composition on permeability.

membranes become more neutral. There is no ready explanation for the absence of this expected trend. Of note is that the slopes for the AVAC membranes are always lower than for the corresponding AVOH membranes. This trend was proved by the results obtained with partially saponified AVAC membranes, which showed an increase in rejection susceptibility to feed concentration as the alcohol content of the copolymer was increased.

The effect of feed concentration on the flux

It was shown that the flux increases for decreasing feed concentration, as does the membrane permeability. This is in contrast with the results predicted by the Donnan exclusion theory. The effect of the feed concentration on the flux in terms of the copolymer compositions was calculated in terms of the slope of the flux vs concentration plot in the concentration region 0,1 mole.dm^{-3} to 0,2 mole.dm^{-3}. The results are shown in Figure 16. Clearly, the copolymer membranes' (both types) flux become more sensitive to a change in feed concentration as the acrylic acid content of the copolymer membrane increased.

C. Developments and discoveries arising from and pendant to the study

Introduction. In this section, a few developments that occurred in the course of this study are reported and discussed. These developments have some importance in the field of dynamically formed membranes. The scope of this study did not, however, allow for the further exploration of these topics.

A High Performance Dynamically Formed Membrane. The state of the art dynamic membrane is the hydrous zirconium oxide-poly(acrylic acid) membrane. The average rejection claimed for these membranes is quoted to be in the range of 88-92 %, which is equal to that found for the commercially used Acrysol A3 polymer under test conditions identical to those used in the course of this study. Fluxes for these membranes are quoted to be in the region of 1500 -2000 *l*md which relates to the test facilities used in the course of these studies to a flux of about 1,70 - 2,20 m*l*/min. From the preceeding sections it is obvious that many of the membranes formed were superior in their rejection and flux capabilities to that of the commercially used Acrysol A3 polymer. The set of results used for comparative purposes is given below.

The results obtained for the commercial polymer Acrysol A3 is given in Table 6.

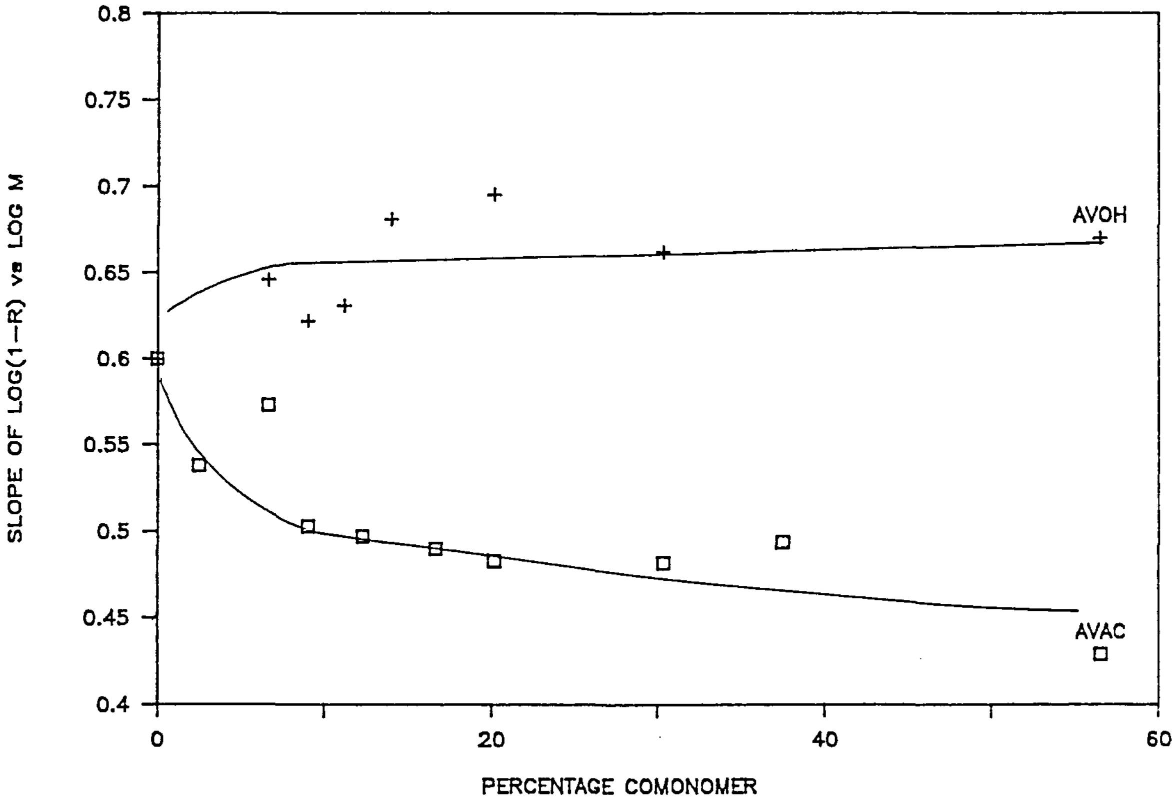

Figure 15. The effect of feed concentration on rejection.

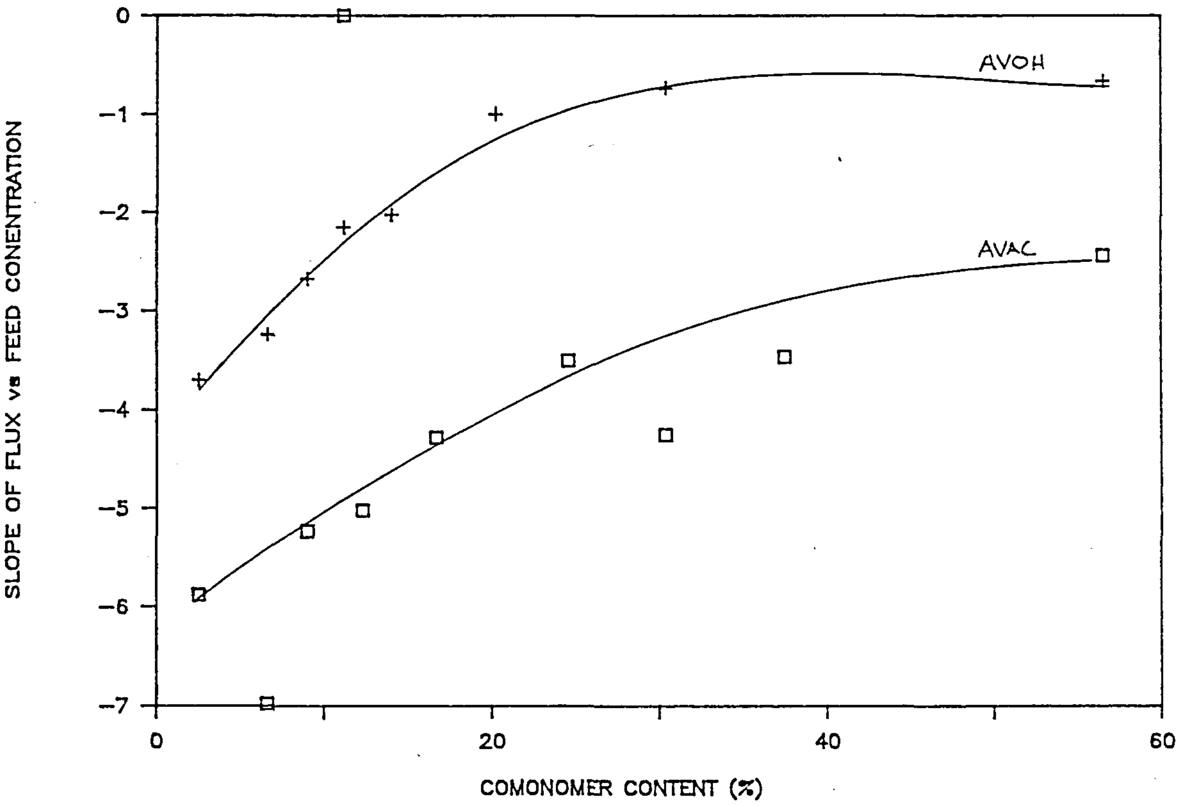

Figure 16. The effect of feed concentration on flux.

TABLE 6: THE PERFORMANCE OF A DYNAMICALLY FORMED HYDROUS ZIRCONIUM IV OXIDE - ACRYSOL A3 MEMBRANE

Time (h)		Rejection (%)	
	R_1	R_2	R_3
1	89,6	89,2	88,8
24	89,8	89,2	89,0
48	90,4	89,0	89,6
		Flux (*l*mh)	
	J_1	J_2	J_3
1	83	87	82
24	79	85	79
48	80	85	76

During the trial polymerization of acrylic acid and vinyl acetate, the reaction was allowed to carry on for a longer period of time, resulting in a copolymer that was not homogeneous. The reaction mixture was that subsequently used to synthesize AVAC 7. The yield in this case was 24,7 % of a copolymer codenamed AVAC 86/2. Of this copolymer, 9,1 g was hydrolyzed for 24 hours in 2 mole.dm^{-3} NaOH at reflux temperature. The yield was quantitative, for polymer AVOH 86/2. As the conversion of the mother polymer was 25 %, the polymer could not be included for the purpose of the study, as the product was not homogeneous. However, a dynamically formed membrane was made using the polymer, and the results were remarkable.The results are given in Tables 7 and 8.

TABLE 7. THE REJECTION BEHAVIOUR OF DYNAMICALLY FORMED HYDROUS ZIRCONIUM OXIDE-AVOH 86/2 MEMBRANES.

Time(h)	Rejection (%)		
	R_1	R_2	R_3
1	99,4	99,7	98,0
5	99,8	99,9	98,5
8	99,4	99,6	98,3
24	99,4	99,6	98,5
48	99,8	99,9	99,1
69	99,5	99,7	99,1
115	99,0	99,1	99,0

TABLE 8: THE EFFECT OF TIME ON THE FLUX BEHAVIOUR OF DYNAMICALLY FORMED HYDROUS ZIRCONIUM OXIDE-AVOH 86/2 MEMBRANES.

Time (h)	Flux (*l*mh)		
	J_1	J_2	J_3
1	94	105	103
5	92	105	100
8	94	100	103
24	96	107	104
48	95	114	110
69	100	114	110
115	105	119	114

It is obvious from the results quoted in Table 7 and 8 that these membranes are far superior in terms of their rejection capabilities to the hydrous zirconium oxide-poly(acrylic acid) membranes. The membranes are quite stable, as can be seen from Tables 7 and 8. Thus these membranes have a definite practical applicability. As the polymer was not homogeneous, it was not possible to include these results in the study conducted. However, titration with a weak base gave a composition of 80 % acrylic acid and 20 % vinyl acetate, in comparison to the 93 % acrylic acid and 7 % vinyl acetate obtained from a similar polymer with the reaction stopped short of 10 % conversion. The composition of the polyner AVOH 86/2 approached, in broad terms, that of AVOH 11, and the slope of the log M vs log (1-R) plots are very similar (about 0,71 as opposed to 0,695). Be that as it may, the good results obtained with these membranes prompted an attempt to treat a real industrial effluent with these dynamically formed AVOH 86/2 membranes.

The treatment of a real industrial effluent with a novel dynamically formed membrane. The industrial effluent obtained was the so-called stripped gas liquor from the SASOL II coal-to-oil plant at Secunda in the Transvaal province of South Africa. The stripped gas liquor (henceforth referred to as SGL) varies in make-up from day to day.

The hydrous zirconium oxide-AVOH 86/2 membrane was formed by the standard procedure. The system was then allowed to equilibrate at the standard test conditions and flux and rejection measurements were taken after one hour. The results are given in Table 9. The feed tank was then drained and flushed. The SGL was introduced and bled through the system and then allowed to fill the feed tank. The system was then allowed to stabilize for 48 hours. The SGL was a dark amber colour and appeared to have a fine suspension. This suspension caused the membrane flux to decrease due to fouling. The flux stabilised at an average of 30 lmh per cell. The flux and rejection was then determined at 5 %, 25 %, 50 %, and 65 % water recovery levels. Feed and permeate samples were sent to the SASTECH division of SASOL for analysis. The results are given in Table 9.

The membranes were, due to their small surface areas, exposed to the SGL for 336 hours. No sign of membrane degradation occurred in this period. The results in Table 9 indicate very good rejection of a widely differing spectrum of constituents. Notable here are substances such as the thiocyanates, acids and hydantoins. Based on the results in Table 9 the membrane AVOH 86/2 has an application in the field of industrial effluent treatment.

Alternative support for dynamic membranes. A variety of support materials have been suggested for use with dynamic membranes. In practice, the support configuration is normally tubular in nature, and the material most commonly used is porous stainless steel tubes. In the laboratory, the support used was Millipore ultrafilters (HA rated 0,45 μm). Porous stainless steel tubes are very expensive. It was decided, as a first attempt, to try to form dynamic membranes in the equipment normally used, at the operating conditions normally used, on a variety of ultrafiltration membranes comprising poly(ether sulfone) microfibres on a polyester backing. Samples of these materials were obtained from Carl Freudenberg (R), tradename VILEDON. The results are given in Table 10. The polyelectrolyte used was the commercially available Acrysol A3.

TABLE 9: REJECTION VALUES OBTAINED WITH SASOL SGL AND DYNAMICALLY FORMED HYDROUS ZIRCONIUM OXIDE - AVOH 86/2 MEMBRANES

Component in SGL	Concentration at water recovery levels (mg/l)				% Removal at water recovery levels			
	5%	25%	50%	65%	5%	25%	50%	65%
Chemical oxygen demand	1 322	1960	2254	3136	94,3	96,7	98,0	97,8
SO_4^{-2}	320				96,9			
Na+	12	12	2	3	99,2	91,7		
K+	0,9	1,5	2,6	3,4	88,9	93,3		
Ca^{+2}	0,5	0,7	0,8	1,0	40,0	42,9	75,0	40,0
Mg^{+2}	0,2	0,3	0,4	0,5	50,0	66,7	75,0	80,0
NH_3 - Nitrogen	271	271	301	337	77,9	94,1	91,7	94,7
Cl^-	85	125	105	225	100,0	100,0	100,0	100,0
F^-	115	145	190	215	99,5	99,7	99,7	99,6
NO_2 - Nitrogen	0,08	0,12	0,32	0,14	75,0	83,3	68,8	71,4
SCN^-	160	180	240	360	97,5	97,2	99,2	98,6
$PO_4^{\equiv}$ phosphorous	0,6	0,6	0,75	0,95	83,3	96,7	86,7	92,6
Phenols	20	10			80,0	100,0		
Acetic acid	70	80	60	30	85,7	96,3	100,0	
Propionic acid	30	20	20		100,0	100,0	100,0	
Dimethyl hydantoin	89	113	164	227	92,1	94,6	99,4	97,8
Methyl-ethyl hydantoin	30	37	68	68	100,0	100,0	100,0	100,0

TABLE 10: THE REJECTION AND FLUX VALUES FOR Zr-ACRYSOL A3 DYNAMIC MEMBRANES FORMED ON FOUR VILEDON NONWOVEN POLYSULPHONE SUPPORT MATERIALS.

1. Support pore size : 15 μm (maximum)

Rejection (%)			Flux (*l*mh)		
1	2	3	1	2	3
46,1*	55,8	20,1	468	506	1287
(79,6)**	(75,4)	(10,6)	(138)	(162)	(1019)
[79,9]***	[74,9]	[9,8]	[138]	[166]	[1019]

2 Support pore size : 15 μm (maximum)

Rejection (%)			Flux (*l*mh)		
1	2	3	1	2	3
57,8	59,0		378	487	
(81,0)	(88,2)		(110)	(100)	
[82,2]	[88,1]		[109]	[98]	

3. Pore support size : 150 μm (maximum)

Rejection (%)			(4 MPa) Flux (*l*mh)		
1	2	3	1	2	3
52,1	53,0	51,2	337	438	438
(81,7)	(82,4)	(37,7)	(196)	(91)	(196)
[81,2]	[82,2]	[47,0]	[92]	[94]	[159]

4. Pore support size : 188 μm (maximum)

Rejection (%)			Flux (*l*mh)		
1	2	3	1	2	3
	48,4	44,4		498	506
	(85,5)	(84,2)		(193)	(189)
	[85,5]	[84,0]		[196]	[189]

The formation and test conditions were standard.
* The unbracketed figures pertain to the hydrous zirconium oxide base membrane.
** The round brackets pertain to the polyelectrolyte membrane 1 hour after formation.
*** The square brackets pertain to the polyelectrolyte membrane 24 hours after formation.

Successful dynamic membranes were formed on all four poly(ether sulphone) ultrafiltration supports. The results obtained with the Acrysol A3 are similar to those obtained with the same polyelectrolyte using a Millipore ultrafilter support. (See Table 6). The success obtained with this alternative support prompted the investigation of a similar support in the tubular form. As the VILEDON material was not available in tubular form, a polyethersulphone membrane cast on a nonwoven polyester support tube was used to form membranes on.

Hydrous zirconium oxide membrane on a tubular ultrafiltration support. The system used was one normally used to evaluate low-pressure thin-film composite membranes. It consisted of six 370 mm tubular test sections in series, each of which was designed to take a tubular polyethersulphone ultrafiltration membrane. The tubular UF membranes were obtained from the Institute for Polymer Science at the University of Stellenbosch.

The hydrous zirconium membranes were formed in the normal fashion, but the flow rate was maintained at 2,1 m/s and the back pressure at 2,0 MPa, as this was the maximum pressure and flow rate that could be obtained with this configuration. The flux and rejection measurements commenced after the system had been rinsed after formation, the pH set at 3,8, the feed concentration at 0,0235 mole.dm^{-3} $NaNO_3$ and the temperature at 30 °C. The results were calculated as an average over the six tubes.

The results are reported in Table 11. The measurements of the individual cells were always close to that of the average.

TABLE 11: THE FLUX AND REJECTION OF HYDROUS ZIRCONIUM OXIDE DYNAMIC MEMBRANES, FORMED ON A TUBULAR UF SUPPORT.

Run time (h)	Rejection (%)	Flux (*l*mh)
1	43,3	
3	39,2	285
12	32,7*	285
14	33,7	285
21	34,3	285
40	35,1	225
59	35,3*	225
60	35,0	225
80	35,4	
97	34,9	
100	36,1	173
145	35,5	150
463	33,9	63
490	33,7	63
513	33,4	62
562	33,4	62
The membranes were then subjected to a continuous supply of municipal tap water.		
587	--	47
630	--	40
754	--	30
781	--	30

* Asterisks indicate results taken after a restart due to a power failure.

The membranes functioned for 562 hours on 0,0235 mole.dm^{-3} $NaNO_3$ feed. After the initial decrease in rejection due largely to two power failures, both of which caused the membranes to stand drying for six hours, rejection of these membranes remained very steady, decreasing only from 35,4 % to 33,4 % in 503 hours of continuous operation. During this period of time, the flux decreased from 5400 *l*md to 1480, the latter being due to membrane fouling. This was doubtlessly caused by the introduction, with time, of microorganisms, dust *etc.* into the test system. After this original period of testing, the membranes were run on municipal tap water for a period of 219 hours. During this time rejection measurements were made, but the feed conductivity was low, about 50 μS/cm, and these measurements were therefore not relevant. The flux decreased markedly during this period of time, dropping from 1480 *l*md to 728 *l*md, a drop of more than 50 %.

This trial proved that satisfactory hydrous zirconium oxide membranes could be formed on tubular UF polyethersulphone supports. The pressure of 2 MPa and the flow rate of 2,1 m/s were substantially lower than the standard 6 MPa and 6 m/s. This augured well for the developement of a low-pressure dynamically formed dual layer membrane, and was well worth further investigation.

Tubular dual layer dynamic membranes on a poly(ether sulfone) support. Following the success obtained with zirconium membranes on poly(ether sulfone) ultrafiltration supports, a dual layer dynamic membrane was then formed on a similar set of membrane supports. The equipment was upgraded to be able to supply a slightly higher flow rate and a higher back pressure rating. The hydrous zirconium oxide base membranes were formed in the normal fashion, with the flow rate maintained at 2,6 m/s and the back pressure at 1,5 MPa. Thereafter the polyelectrolyte membrane in question was formed in the normal fashion, using the same experimental parameters used for the zirconium membrane formation. Two different polyelectrolytes were used, i.e poly(acrylic acid) and AVOH 12. The latter polyelectrolyte was also used to form a dynamic membrane on a porous stainless steel support tube. The results are quoted in Table 12.

TABLE 12: THE PERFORMANCE OF DUAL LAYER DYNAMICALLY FORMED MEMBRANES ON TUBULAR UF SUPPORT MATERIALS

Polyelectrolyte	Pressure (MPa)	Flow rate (*l*/h)	Rejection (%)	Flux (*l*mh)
PAA-88/1	2,0	1200	71,0	
	2,5	1200	77,0	
	3,0	1200	80,0	63
AVOH 12	2,0	1200	76,6	
	2,5	1200	81,4	
	3,0	1200	83,8	42
AVOH 12*	2,0	1200	61,2	76
	2,5	1200	60,7	92

* Asterisk denotes membrane formed on porous stainless steel substrate.

The above membranes were formed at 1,5 MPa and approximately 3,1 m/s crossflow velocity. Reasonably good results were obtained. If the crossflow velocity could be increased to 6 m/s and the back pressure to above 5 MPa, dynamic membranes with performances equal to or better than those formed on porous stainless steel tubes could be expected. The rejections obtained were in fact higher than that obtained when using the porous stainless steel supports (see Table 11), although the fluxes were lower for the membranes formed on the poly(ether sulfone) supports than for those formed on the porous stainless steel.

Dynamic membranes can sucessfully be formed on tubular poly(ether sulfone) supports. Results obtained indicate that the performance figures could equal that obtained on porous stainless steel support at normal operating pressures and flow rates, and more research in this field is warranted.

Tubular dual layer dynamic membranes on a poly(ether sulfone) support: The effect of higher formation pressure. Although the tubular configuration used could not be changed to obtain the cross-flow velocitiy required, *i.e* 6 m/s, an attempt was made to form dual layer dynamic membranes at higher pressures than formerly attempted. The results are given in Table 13.

TABLE 13: FORMATION OF DYNAMIC MEMBRANES ON POLY(ETHER SULPHONE) SUBSTRATE MEMBRANES. THE EFFECT OF HIGHER FORMATION PRESSURE

Membrane	Pressure (MPa)	Flow rate (*l*/h)	pH	Rejection (%)	Flux (*l*mh)
Zr-I	2,50	1200	3,60	17,0	-
Zr-II	2,50	1200	3,60	14,7	-
Zr-III	2,50	1200	3,60	14,7	-
PAA-I	4,00	1200	7,00	87,0	70
PAA-II	4,00	1200	7,00	88,4	56
PAA-III	4,00	1200	7,00	88,3	55

Rejection and flux values obtained with poly(acrylic acid) (PAA) membranes at formation pressures of 4 MPa and cross-flow velocity of 2,7 m/s approach that obtained at 6 m/s cross-flow velocity and 6 MPa pressure on tubular stainless steel supports *(5)*. Refining the technique and using other polyelectrolytes led to even better results. These are given in Table 14.

TABLE 14: PERFORMANCE OF DUAL LAYER MEMBRANES ON SYNTHETIC SUBSTRATES

Membrane	pH	Formation pressure (kPa)	Flow rate (m/s)	Rejection (%)	Flux (l/m^2h)
Zr-I	3,6	2500	2,63	32,4	140
Zr-II	3,6	2500	2,63	34,8	150
Zr-III	3,6	2500	2,63	30,5	154
Zr-IV	3,6	3000	2,63	35,4	260
Zr-V	3,6	3000	2,63	33,7	250
Zr-VI	3,6	3000	2,63	33,9	235
Zr-I-PAA	7,0	3000	2,63	87,6	76
Zr-II-PAA	7,0	3000	2,63	88,6	71
Zr-III-PAA	7,0	3000	2,63	88,3	68
Zr-IV-AVOH	7,0	3000	2,63	91,8	98
Zr-V-AVOH	7,0	3000	2,63	88,8	93
Zr-VI-AVOH	7,0	3000	2,63	89,6	86

PAA: poly(acrylic acid)
AVOH: poly(acrylic acid-co-vinyl alcohol)

Application of dynamic membrane chemistry to other membrane uses. The use of AVAC copolymers as low rejection, low-pressure membranes were investigated. Results on individual 12,5 mm diameter tubes give encouraging results. Results are given in Table 15.

TABLE 15: MEMBRANE PERFORMANCE OF LOW PRESSURE MEMBRANES

Membrane	Pressure (MPa)	Electrolyte (500 ppm)	Rejection (%)	Flux (lmh)	Operating pH
UF/RO 1	0,5	$NaNO_3$	21,3	59	3,0
UF/RO 2	0,5	$NaNO_3$	21,6	40	3,0
UF/RO 3	0,5	$NaNO_3$	16,7	73	3,0
UF/RO 1	0,5	$NaNO_3$	47,8	45	6,7
UF/RO 2	0,5	$NaNO_3$	54,4	26	6,7
UF/RO 3	0,5	$NaNO_3$	34,0	51	6,7
UF/RO 1	0,5	$MgSO_4$	56,1	34	6,5
UF/RO 2	0,5	$MgSO_4$	60,4	24	6,5
UF/RO 3	0,5	$MgSO_4$	31,1	31	6,5

SUPPLY OF POLYMERS TO THE CSIR AND THE UNIVERSITY OF NATAL.

During the course of 1988 a total of 6 polymers were sent to the CSIR for evaluation. No results have been recieved. Four polymers were sent to the University of Natal for evaluation. Two polymers were evaluated, and the results are given in Table 16.

The initial results are encouraging, although these membranes do not show the same storage stability as dynamically formed Zr-PAA membranes.

TABLE 16: HYDROUS ZIRCONIUM (IV) OXIDE POLYELECTROLYTE MEMBRANES FORMED AND EVALUATED AT THE UNIVERSITY OF NATAL.

Date	Membrane	Inlet Pressure (kPa)	Flow Rate (m/s)	Flux (l/m^2h)	Rejection (%)	Feed Conductivity (mS/cm)
8/11/88	Zr*	6000	4,3	588	39	2,46
9/11/88	Zr-PAA*	6000	4,3	195	80	2,30
9/11/88	Zr-PAA*	3000	4,6	75	70	2,30
14/11/88	Zr**	4000	4,5	576	40	2,68
15/11/88	Zr-PAA**	4000	4,4	159	78	2,24
	Zr-PAA**	3000	4,8	114	74	2,23
	Zr-PAA**	6000	4,1	264	80	2,23
29/11/88	Zr	4000	4,5	636	41	2,45
30/11/88	Zr-IPR[1]	4000	4,5	105	85	2,32
	Zr-IPR[1]	6000	4,3	165	88	2,34
19/12/88	Zr-IPR[2]	4000	4,4	38	89	2,43
	Zr-IPR[2]	6000	4,3	57	90	2,42
22/12/88	Zr-IPR[2r]	6000	4,4	70	82	2,34

* Tube pretreated with precipitated hydrous zirconia at 4000 kPa, Zr and Zr-PAA membranes formed at 6000 kPa.

** Tube pretreated with precipitated hydrous zirconia at 4000 kPa, Zr and Zr-PAA membranes formed at 4000 kPa.

[1] Copolymer of acrylic acid and vinyl acetate. Tube pretreated with precipitated hydrous zirconia at 4000 kPa, Zr and Zr-IPR membranes formed at 4000 kPa.

[2] Fully hydrolyzed copolymer.

[2r] Retested after 3 days in storage.

CONCLUSIONS

1. A number of acrylic acid copolymers were synthesized that, when used as dynamic membranes, gave, under identical laboratory conditions, better salt rejection than poly(acrylic acid) membranes.

2. The use of cheap plastic ultrafilters (poly(ether sulfone) on polyester fabric) as dynamic membrane subtrates have been sucessfully demonstrated.

3. The use of dynamic membrane chemistry, developed during this research, to make low-rejection, low pressure membranes have been demonstrated. This is an area that needs to be investigated fully.

4. The research has led to a much better understanding of the way in which dynamic membranes function.

5. The research into the synthesis of polymers for dynamic membranes is, under the present set of circumstances, complete. Changes to polymers can be made as the process of industrialisation dictates.

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(ii) "Acrylic acid copolymers as dynamic membrane polyelectrolytes: The effect of copolymer composition on membrane performance", A.J. van Reenen and R.D. Sanderson.

(iii) Self-crosslinking polyelectrolytes as dynamic membranes", S. Gerber and A.J. van Reenen.

PATENTS

1 S.A. Patent 86/4070 "Dynamic membranes"; R.D. Sanderson, N.A. Dowler and A.J. van Reenen.

2. European patent 87/30429.4 "Dynamic membranes"; R.D. Sanderson, N.A. Dowler and A.J. van Reenen.

3. U.S.A patent application 053,333 "Dynamic membranes"; R.D. Sanderson, N.A. Dowler and A.J. van Reenen.

FINAL REPORT

RESEARCH AND DEVELOPMENT OF POLYMEYERS FOR THE FORMATION OF DYNAMIC MEMBRANES AND THE EVALUATION THEREOF FOR THE TREATMENT OF INDUSTRIAL EFFLUENTS

PART 3

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PROJECT: Research on the development of polymers for the formation of dynamic membranes and the evaluation thereof for the treatment of industrial effluents

SUMMARY

Ten novel polymers developed by the Institute for Polymer Science (IPS) University of Stellenbosch, Stellenbosch were tested for suitability in DWT membranes . All of them formed membranes, but the Robs values turned out to be rather low, and cover a wide range with the best membranes not exceeding 67 %. Measured against the performance of existing membranes, the Robs is probably too low to warrant application in practice.

The flux rates of these membranes are generally high. They could possibly, therefore, be suited as ultrafiltration membranes provided a suitable low cost module can be employed with them. Our research has been limited to porous stainless steel supports which are very costly. This makes any economic ultrafiltration application difficult.

In general it can be concluded that the IPS polymers are not as well suited as some other materials we have tested, and seem less suited to the DWT process than they are to the ORNL process. They can therefore not serve on their own as the basis for further testing at factory sites. However, two of the IPS polymers (4 and 8) show enough promise as ultrafiltration membranes to warrant further factory site tests provided the cost of such tests can be kept low by conducting them in conjunction with other tests as we envisage in respect of the DWT-Technifin technology during 1989. For this eventuality this project has been extended through to December 1989.

Since these results indicate that the DWT membrane technology imposes very definite structural requirements on the polymer, it is recommended that no further polymers based on the ORNL technology should be investigated by the DWT. A more specific approach aimed at the detail of the DWT process is necessary.

1 INTRODUCTION

An interesting and promising group of hyperfiltration and ultrafiltration membranes are the so-called "dynamically formed" or "dynamic membranes" pioneered by the group at Oak Ridge National Laboratory (Marcinkowsky, Kraus, Phillips, Johnson & Shor, 1966). They belong to the large family of reverse osmosis membranes, but differ from them distinctly in terms of their method of formation and regeneration. Dynamic membranes are formed in situ in that a solution containing an additive is sent past a porous support at high pressure. A thin layer of additive collects at the surface of the porous support and creates the membrane.

Dynamic membranes have also been successfully formed from species already present in the feed solution (Perona, Butt, Fleming, Mayr, Spitz, Brown, Cochran, Krause & Johnson, 1967; Bansal & Wiley, 1974). For example, Perona et al (1967) demonstrated that the lignosulphates present in spent sulphite liquors produced dynamic membranes on porous carbon and ceramic substrates, which then ultrafiltered coloured matter and sugars from the solution. Dynamic membranes have also been generated with sewage water and surface water feeds (Savage, Bolton, Phillips, Kraus & Johnson, 1969). Also membrane fouling, caused by the build-up of deposits on the high pressure side of a semi-permeable membrane, could be considered as an uncontrolled dynamic membrane formation (Drioli, 1977), however, with predominantly negative effects on the separation process.

Thus whether we deal with dynamic membranes by choice or accident, it is important to distinguish them as a distinct class within the family of reverse osmosis membranes. For the purpose of this study, emphasis will be placed on membranes which are deliberately formed and which offer the advantage of in situ formation and regeneration.

Research on dynamic membranes at the Division for Water Technology Research has led to the development of several new dynamic membranes which can be formed and used at relatively low pressures (about 2 MPa) and which can tolerate relatively high temperatures (above 60 °C). The membranes show promise as potential candidates for the treatment of hot industrial effluents and also provide the possibility of using dynamic membranes in low pressure support elements. Limited testing has been done with the new membranes and a limited number of membrane materials have been used mainly in conjunction with sintered stainless steel porous supports.

In order to exploit the new technology more fully, and to enable us to specify a broad but specific patent, it was necessary to increase the base of the technology by investigating the suitability of a broad range of membrane materials. With this in mind, this project was initiated with objectives as stated in the next section.

The DWT has built up its own dynamic membrane technology. Two other groups, viz the Pollution Research Group (Department of Chemical Engineering, University of Natal, Durban) and the Institute for Polymer Science (IPS) specialized in ORNL (Oak Ridge National Laboratory) membranes (Johnson, Minturn & Wadia, 1972). The IPS has developed a number of interesting and novel polymers for ORNL membranes; a project which is continuing. It was mutually agreed at the outset of this project that these polymers should ideally also be tested in the context of DWT technologies. These polymers were thus not tailored specifically for our application and the test results reported here must therefore be seen against this background.

The DWT technology is owned by TECHNIFIN (Pty) Ltd and is kept confidential at this stage. While all experimental results are included in this report, this limits the detail that we may include in our discussion.

2 PROJECT OBJECTIVES

The objectives of the project were:

2.1 To determine the suitability of the polymers from the Institute for Polymer Sciences for dynamic membrane formation according to the DWT technology on sintered steel supports;

2.2 To undertake tests at factory sites with any promising membranes which could be formed with the IPS polymers.

3 EXPERIMENTAL

3.1 MEMBRANE SUPPORT MODULE

The membranes were formed on the inside surfaces of Mott porous sintered stainless steel tubular supports that had a nominal pore diameter of 0,5 µm, a length of 910 mm, an inner diameter of 9,5 mm and an outer diameter of 12,7 mm. The individual porous tube elements were permanently mounted in tubular stainless steel housings.

3.2 DYNAMIC MEMBRANE UNIT

The dynamic membrane reverse osmosis unit shown schematically in Figure 1 was used. All the metal surfaces in the loop were of 316 stainless steel.

The feed solution was drawn from a 100 litre feed tank by a Hydracell D10 high-pressure, low-volume pump and forced, under pressure, on the inside of the tubes past the membranes. Linear flow velocities were monitored by means of a flow meter. Pressure differentials across the membranes were monitored using inlet and outlet pressure indicators. The temperature of the test solutions was controlled by means of a heat exchanger with an external cooling circuit.

The pressure and linear flow velocities were regulated by control valves and a flow by-pass. Permeate, concentrate and by-pass flows were all returned to the feed tank in order to maintain a constant feed composition.

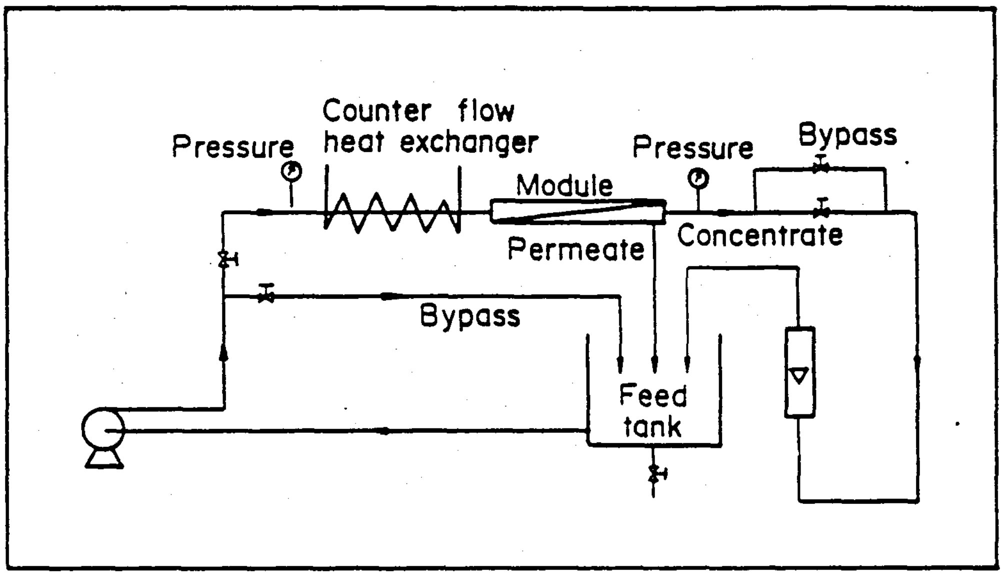

FIGURE 1: Flow diagram of dynamic membrane unit

3.3 MEMBRANE FORMATION PROCEDURE

The membranes were formed from Pol1 to Pol10 (see Table 1) according to the standard DWT procedure at 3 MPa. Further details cannot be disclosed at this stage because of patent considerations.

3.4 MEMBRANE TESTING PROCEDURES

3.4.1 Standard test

Operational conditions during testing were kept constant at pH 7, 30 °C, 3 MPa and 4,5 m/s cross flow velocity. The test solution was 0,05 M NaCl (2920 mg/l) for Pol1 and Pol2 and for Pol3 to Pol10 it was 0,05 M $NaNO_3$ (4249,5 mg/l). Measurements were taken at about 2 hours after start-up for the calculation of the % Robs (% observed salt rejection) and flux rate ($l/m^2/h$).

3.4.2 Pressure scan

The pressure scan was conducted under conditions where the pressure was varied in the following sequence at 60 min intervals: 3, 1, 2, 3, 4, 3 MPa. The other operational conditions were kept constant and the same as for the standards test (3.4.1). Measurements were taken 60 min after setting the new pressure conditions.

3.4.3 pH scan

The pH scan was carried out under conditions where the pH was allowed to vary step-wise at 60 min intervals as follows: 7, 4, 5, 6, 7, 8, 9, 7. The other operational conditions were kept constant and the same as for the standard test (3.4.1). Measurements were taken 60 min after setting to a new pH took place.

3.4.4 Concentration scan

The concentration scan was conducted under conditions where the level of the $NaNO_3$ concentration was varied at 60 min intervals as follows: 850, 2124,8, 4249,5, 6374,3, 8499,0, 12748,5 4249,5 mg/l. The other operational conditions were kept constant and the same as for the standard test (3.4.1). Measurements were taken 60 min after the concentration was changed to a new level.

3.5 POLYMERS

Ten polymers, numbered Pol1 to Pol10 in the table below, were received from IPS between 1986 and 1988. The results in respect of Pol1 - Pol4 have been reported previously, but are included for reference in this report.

POLYMERS

Polymer No.	Polymer Symbol (Stellenbosch)	Polymer description
1	MAVA	[poly(maleic acid-alt-vinyl acetate)]
2	MAVOH	[poly(maleic acid-alt-vinyl alcohol)]
3	PAA/VOH-86/2B	[poly(acrylic acid-co-vinyl alcohol)]
4		[poly(maleic acid-alt-acrylic acid)]
5	AVAC16	[poly(acrylic acid-co-vinyl acetate)]
6	AVOH16	[poly(acrylic acid-co-vinyl alcohol)] 10 % solution
7	AVAC15	[Acrylic acid - vinyl acetate copolymer]
8	AVAC7	[poly(acrylic acid-co-vinyl acetate)]
9	AVOH7	[poly(acrylic acid-co-vinyl alcohol)] hydrolysis product of AVAC7 10 % solution
10	AVOH15	[poly(acrylic acid-co-vinyl alcohol)] hydrolysis product of AVAC15 10 % solution

4 RESULTS AND DISCUSSION

The results for the membranes formed with Pol1 - Pol10 in respect of the standard test and the pressure, pH and concentration scans are given in Table 1 to 31 and Figures 2 to 31.

TABLE 1A: Performance of Membranes according to Standard Test

Polymer	Tube No	Robs (%) Readings	Robs (%) Average	Flux (l/sq.m.hour) Readings	Flux (l/sq.m.hour) Average
1	43	41.50		345.83	
1	51	44.70	43.10	293.75	319.79
2	25	62.80		116.67	
2	46	53.20	58	214.58	165.63
3	64	34.48		267.38	
3	78	27.59	31.04	372.58	319.98
4	54	64.60		328.75	
4	59	66.67	65.64	280.53	304.64
5	37	42.86		153.42	
5	52	37.36	40.11	219.17	186.30
6	1	9.89		473.40	
6	47	7.69	8.79	578.60	526
7	38	31.52		433.96	
7	72	20.65	26.09	475.25	454.61
8	43	66.30		355	
8	77	67.39	66.85	328.75	341.88
9	21	48.91		302.46	
9	52	51.10	50.01	276.17	289.32
10	23	20.65		539.17	
10	28	18.48	19.57	473.33	506.25

STANDARD TEST CONDITIONS - Pol1 - Pol10

Date	1986 - 1988	Pressure (MPa)	3
Salt	NaCl(Pol1+2)	Cfv (m/s)	4.5
Salt Conc (mg/l)	2920	pH	7
Salt	NaNO3		
Salt Conc (mg/l)	4249.5		

+92% 6000 lwd. 3MPa DWT.
4.5 m/s

TABLE 1B Robs in ascending order

Polymer	Robs (%) Average	Flux(l/m²/h) Average
6	8.79	526.00
10	19.57	506.25
7	26.89	454.61
3	31.04	319.98
5	40.11	186.30
1	43.10	319.79
9	50.01	289.32
2	58.00	165.63
4	65.64	304.64
8	66.85	341.88

In this report we compare all the test results with a view to select promising polymer membrane combinations for possible further testing at factory sites. A Robs (% observed salt rejection) of about 80 % and a flux rate (l/m²/h) of 200 l/m²/h under standard test conditions (3.4.1) were considered by us to be the minimum requirement before further testing is warranted. This criterion was selected on the basis of results that we normally get with the DWT technology. A comparison of the membranes is made under different test conditions. We have chosen a pressure scan, pH scan, and a concentration scan, because they collectively lead to a broad and sensitive characterization of dynamic membrane behaviour.

All our experimental results have been included in this report. Limited discussion of each polymer's performance as regards pH, pressure and concentration scans is, however, included in the report, mainly because little is to be gained from such discussions.

Standard test

As can be seen in Tables 1A and 1B, the different polymers result in a range of membranes which differ distinctly in respect of their flux rates and Robs. The lowest Robs is approximately 9% and the highest approximately 67%. The flux rates are relatively high, probably because of the low Robs.

Pressure scan

The flux rate for all the membranes is, as expected, highly dependent on the operating pressure and increases with increasing pressure. The relationship between flux rate and pressure varies from membrane to membrane. The Robs is less dependent on pressure, particularly at pressures above 2 MPa.

pH Scan

The relationship between pH and Robs and between pH and flux differs between memranes, but follows the expected general pattern, namely an increase in Robs as pH increases and a simultaneous decrease in flux rate. The steepest slopes in respect of Robs vs pH are associated with the higher rejection membranes e.g. Po14 and Po18 and is thus probably related to the charge density within the rejecting layer.

Concentration scan

The flux rate of all the membranes is only slightly dependent on the feed concentration. A slight decrease in flux rate is associated with increased salt concentration.

Robs on the other hand is greatly influenced by the salt concentration. The lower rejection membranes show a particularly steep decline in Robs with increased salt concentration, e.g. Po17 and Po110.

5 CONCLUSIONS

- All the polymers formed membranes. The % Robs values are, however, rather low and cover a wide range with the best membranes not exceeding 67 %. Measured against the performance of existing membranes, the % Robs is probably too low to warrant practical application.

- The flux rates of these membranes are in general high. They could possibly, therefore, be suited as ultrafiltration membranes provided a suitable low cost module can be employed with them. Up to now the research was limited to porous stainless steel supports which are very costly. This makes any economic application difficult unless a particular niche is addressed where recovery of valuable products could contribute to the economics of the process.

- The research with the IPS polymers, covering a broad spectrum of chemical structures, has given us confidence in our understanding of the potential of this technology. Unfortunately we cannot elaborate on the comparisons with the DWT membranes, as this technology is now the property of TECHNIFIN (Pty) Ltd.

- In general it can be concluded that the IPS polymers are not as well suited as some other materials we have tested, and seem less suited to the DWT process than they are to the ORNL process. They can therefore not serve on their own as the basis for further testing at factory sites. However, two of the IPS polymers (4 and 8) show enough promise as ultrafiltration membranes to warrant further factory site tests provided the cost of such tests can be kept low by conducting them in conjunction with other tests as we envisage in respect of the DWT-Technifin technology during 1989. For this eventuality this project has been extended through to December 1989.

6 RECOMMENDATIONS

- Since these results indicate that the DWT membrane technology can only be developed if very definite structural requirements of the polymer are met, it is recommended that no further polymers based on the ORNL technology be investigated by the DWT. A more specific approach aimed at the detail of the DWT technology is necessary. However, due to the restricted nature of the DWT technology, special agreements will have to be entered into before any new research contracts in this respect can be initiated.
- It is recommended that tests with either Po14 or Po18 be conducted at a factory site during 1989 by the DWT as part of their own test programme, provided a practical and mutually satisfying arrangement can be made with the WRC.
- The DWT dynamic membrane technology as such has not been tested extensively at factory sites, nor has it been matched with a low cost porous support system. It is recommended that consideration be given to the formulation of a new research project agreement between DWT and WRC which is aimed at the attaining of these goals, particularly in view of the fact that the IPS is presently developing a low cost porous support system.

7 WORKING PROGRAMME: 1989

The project period has been extended until December 1989 in order to accommodate a possible factory site test of the most promising membrane, provided a mutually satisfactory arrangement to achieve this can be made. At this stage it is not possible to give a detailed outline of such a possible test.

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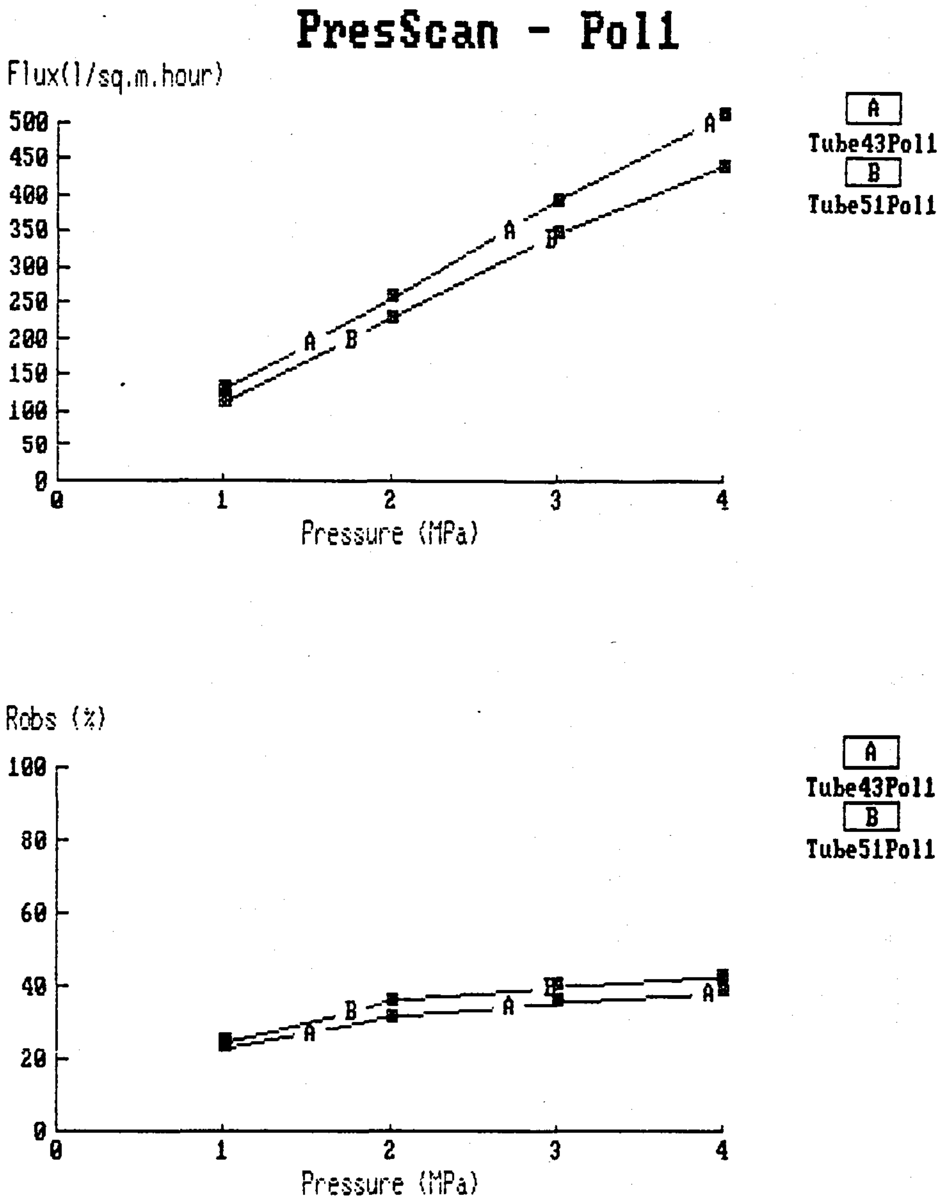


FIGURE 2: Performance vs Pressure during Pressure Scan Poll Membrane

EXPERIMENTAL CONDITIONS - PresScan - Poll

Date	86-08-13	pH	7
Tubes	43/51	Temperature (°C)	30
Salt	NaCl	Cfv (m/s)	4.5
Salt Conc (mg/l)	2920	Direction of Scan	1 —> 4

TABLE 2: Performance of Membranes at Different Pressures

Data for Figure 2 - Pressure Scan - Poll

Poll	Flux (l/sq.m.hour)		Robs (%)	
Pres\Tube	43	51	43	51
3*	381.35	328.75	36.26	40.66
1	129.31	111.78	23.08	24.18
2	254.23	227.93	31.52	35.87
3	390.12	346.28	35.48	39.78
4	508.47	438.33	38.30	42.55
3*	363.82	315.60	36.17	40.43

EXPERIMENTAL CONDITIONS - PresScan - Poll

Date	86-08-13	pH	7
Tubes	43/51	Temperature (°C)	30
Salt	NaCl	Cfv (m/s)	4.5
Salt Conc (mg/l)	2920	Direction of Scan	1 --> 4

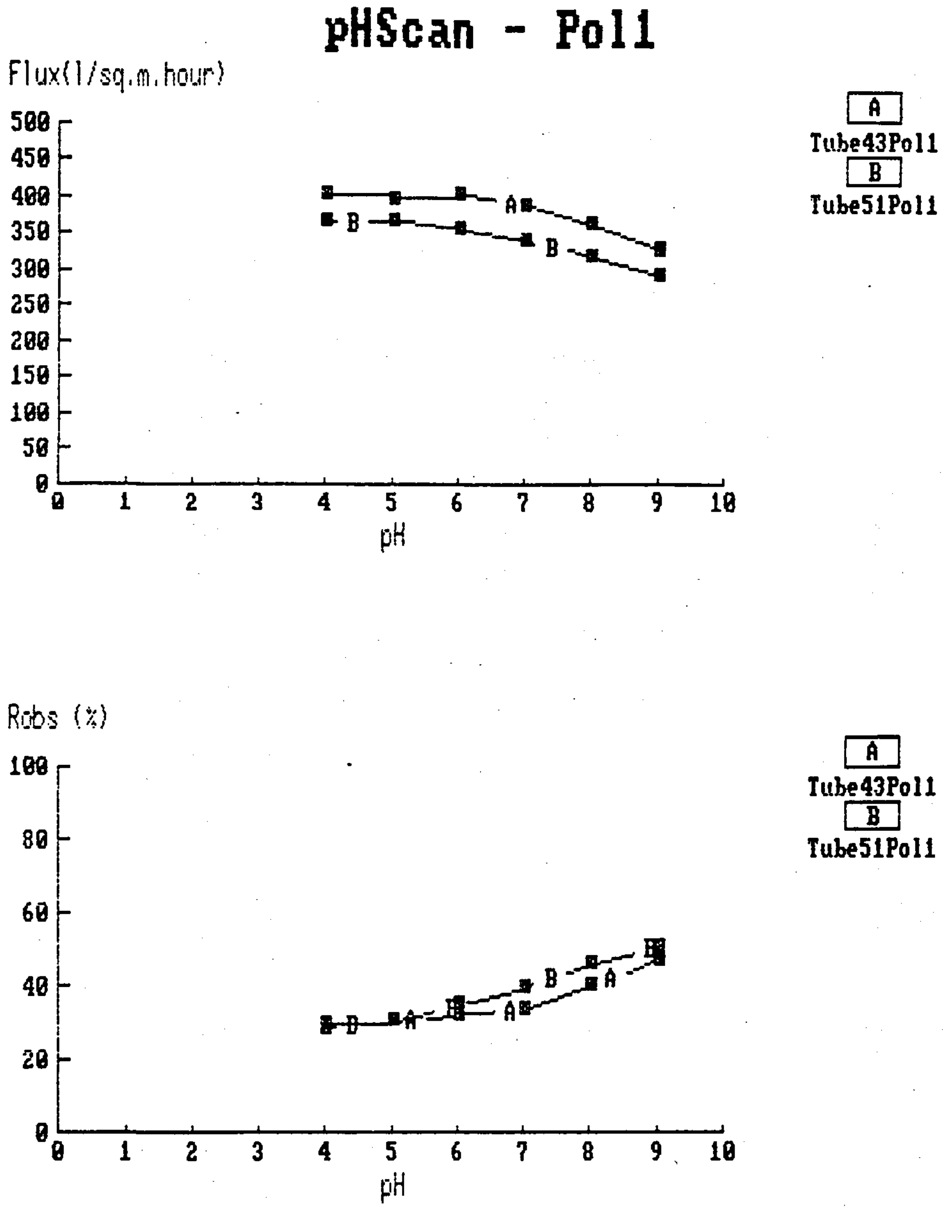


FIGURE 3: Performance vs pH during pH Scan
Poll Membrane

EXPERIMENTAL CONDITIONS - pHScan - Poll

Date	86-08-15	Pressure (MPa)	3
Tubes	43/51	Temperature (°C)	30
Salt	NaCl	Cfv (m/s)	4.5
Salt Conc (mg/l)	2920	Direction of Scan	4 —> 9

TABLE 3: Performance of Membranes at different pH

Data for Figure 3 - pHScan - Poll

Poll	Flux (l/sq.m.hour)		Robs (%)	
pH\Tube	43	51	43	51
7*	394.50	346.28	34.15	39.02
4	398.88	363.82	29.76	28.57
5	394.50	363.82	30.12	30.12
6	398.88	350.67	32.14	34.52
7	385.73	337.52	33.33	39.29
8	359.43	315.60	40	45.88
9	324.37	289.30	47.06	50.59
7*	350.67	319.98	39.53	43.02

EXPERIMENTAL CONDITIONS - pHScan - Poll

Date	86-08-15	Pressure (MPa)	3
Tubes	43/51	Temperature (°C)	30
Salt	NaCl	Cfv (m/s)	4.5
Salt Conc (mg/l)	2920	Direction of Scan	4 —> 9

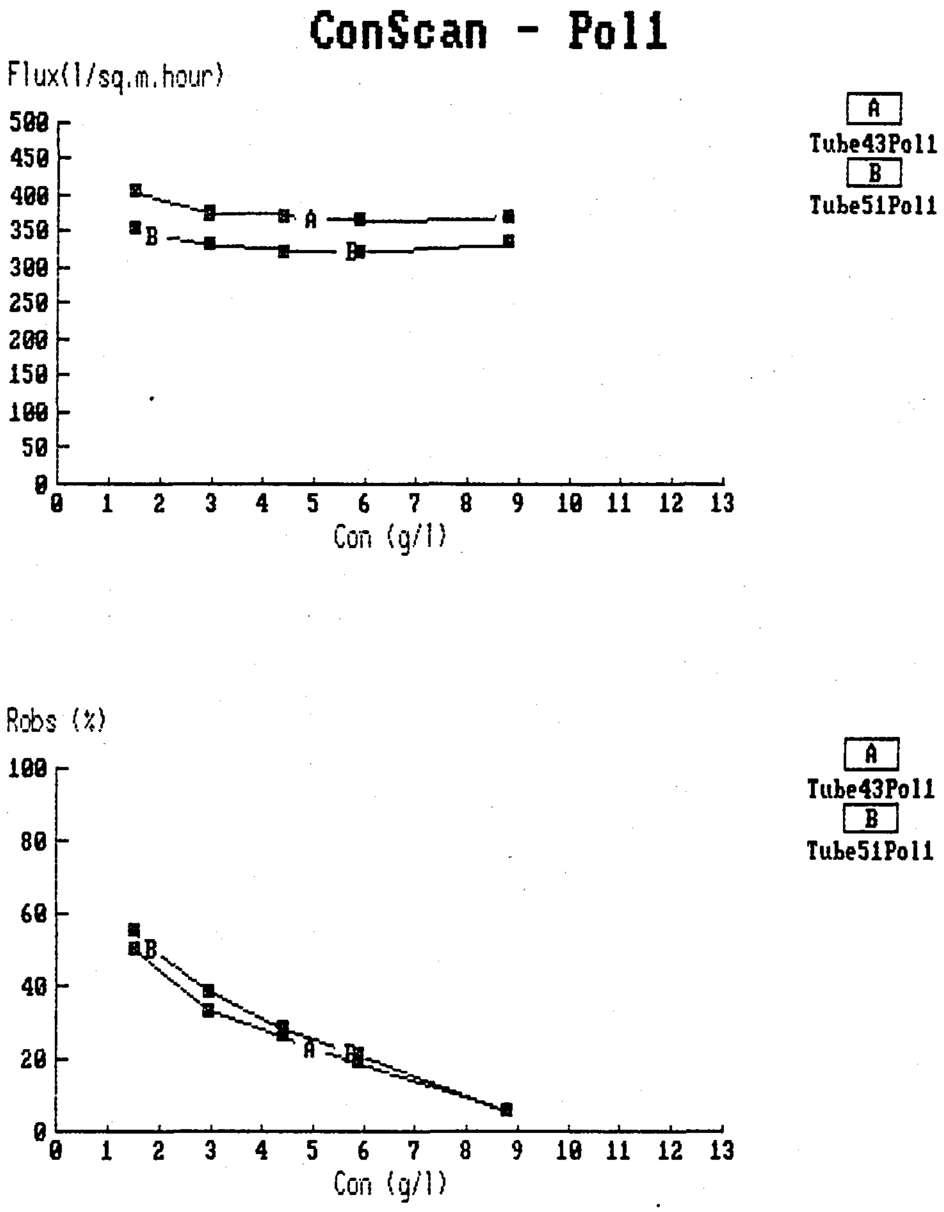


FIGURE 4: Performance vs Concentration during ConScan Poll Membrane

EXPERIMENTAL CONDITIONS - ConScan - Poll

Date	86-08-14	Pressure (MPa)	3
Tubes	43/51	Temperature (°C)	30
Salt	NaCl	Cfv (m/s)	4.5
Salt Conc (g/l)	1 - 9	pH	7
Direction of Scan	1 —> 9		

TABLE 4: Performance of Membranes at different Concentrtions

Data for Figure 4 - Concentration Scan

Poll	Flux (1/sq.m.hour)		Robs (%)	
Con\Tube	43	51	43	51
1.46	403.27	350.67	50	54.55
2.92	372.58	328.75	32.99	38.14
4.38	368.20	319.98	25.64	28.21
5.84	363.82	319.98	18.33	20.83
8.76	368.20	333.13	5.06	5.06
2.92*	385.73	337.52	27.42	31.45

EXPERIMENTAL CONDITIONS - ConScan - Poll

Date	86-08-14	Pressure (MPa)	3
Tubes	43/51	Temperature (°C)	30
Salt	NaCl	Cfv (m/s)	4.5
Salt Conc (g/l)	1 - 9	pH	7
Direction of Scan	1 —> 9		

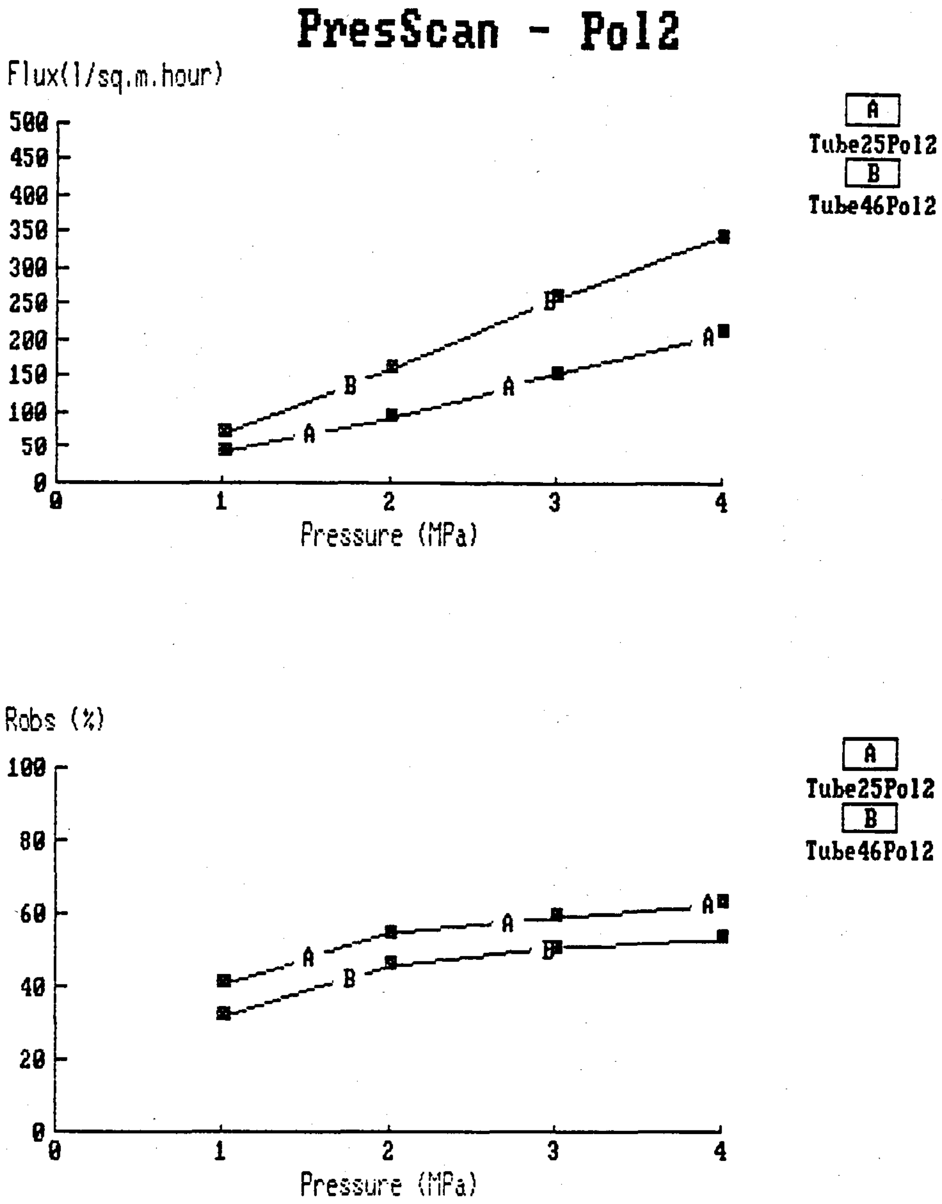


FIGURE 5: Performance vs Pressure during Pressure Scan
Pol2 Membrane

EXPERIMENTAL CONDITIONS - PresScan - Pol2

Date	86-08-13	pH	7
Tubes	25/46	Temperature (°C)	30
Salt	NaCl	Cfv (m/s)	4.5
Salt Conc (mg/l)	2920	Direction of Scan	1 —> 4

TABLE 5: Performance of Membranes at Different Pressures

Data for Figure 5 - Pressure Scan - Pol2

Pol2	Flux (l/sq.m.hour)		Robs (%)	
Pres\Tube	25	46	25	46
3*	140.27	241.08	59.34	50.55
1	43.83	70.13	40.66	31.87
2	92.05	157.80	54.35	45.65
3	153.42	258.62	59.14	50.54
4	210.40	341.90	62.77	53.19
3*	135.88	227.93	59.57	51.06

EXPERIMENTAL CONDITIONS - PresScan - Pol2

Date	86-08-13	pH	7
Tubes	25/46	Temperature (°C)	30
Salt	NaCl	Cfv (m/s)	4.5
Salt Conc (mg/l)	2920	Direction of Scan	1 —> 4

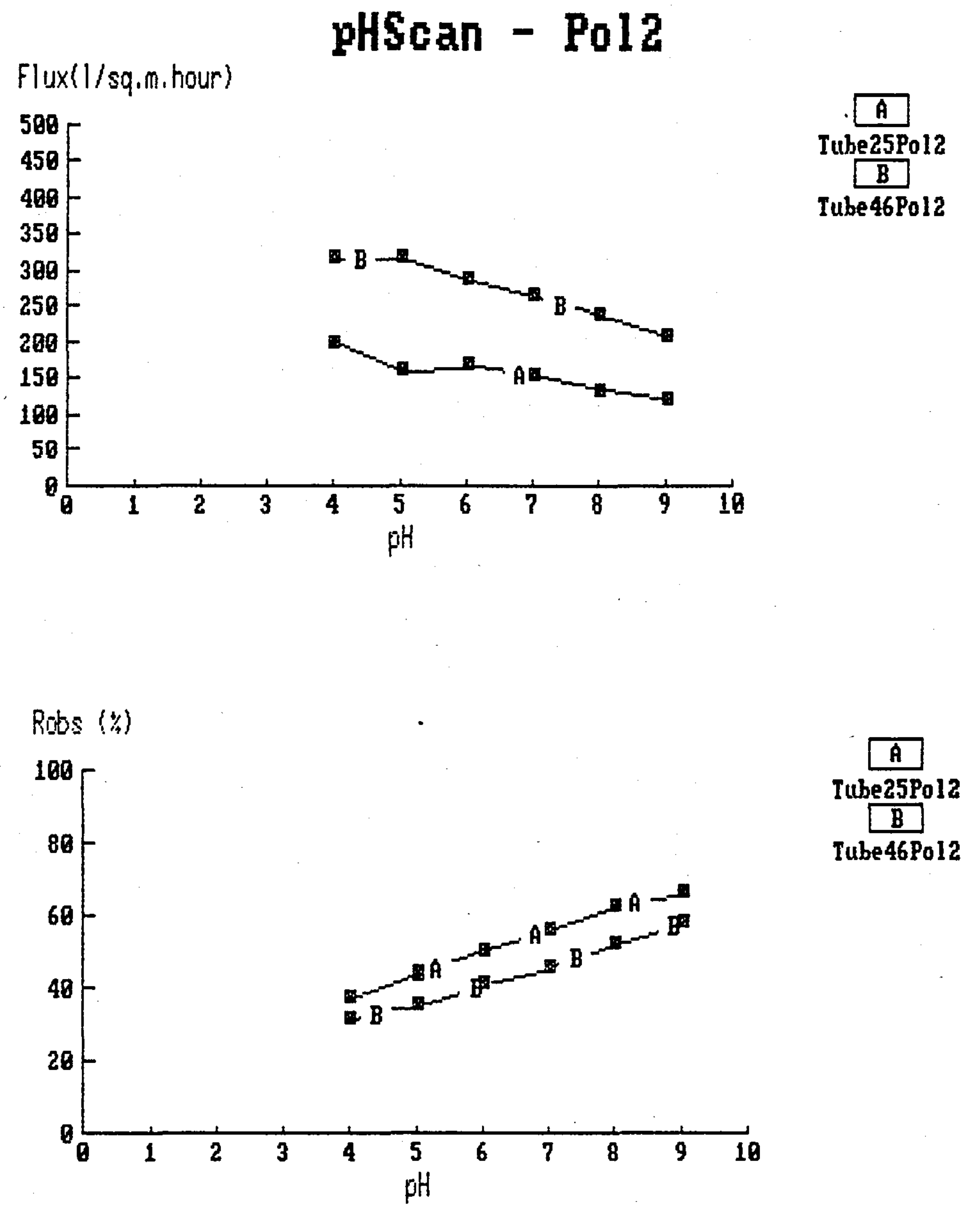


FIGURE 6: Performance vs pH during pH Scan
Po12 Membrane

EXPERIMENTAL CONDITIONS - pHScan - Po12

Date	86-08-15	Pressure (MPa)	3
Tubes	25/46	Temperature (°C)	30
Salt	NaCl	Cfv (m/s)	4.5
Salt Conc (mg/l)	2920	Direction of Scan	4 —> 9

TABLE 6: Performance of Membranes at different pH

Data for Figure 6 - pHScan - Pol2

Pol2	Flux (1/sq.m.hour)		Robs (%)	
pH\Tube	25	46	25	46
7*	149.03	249.85	60.98	50
4	197.25	315.60	36.90	30.95
5	157.80	315.60	43.37	34.94
6	166.57	284.92	50	40.48
7	153.42	263.00	55.95	45.24
8	131.50	236.70	62.35	51.76
9	118.35	206.02	65.88	57.65
7*	131.50	223.55	63.95	54.65

EXPERIMENTAL CONDITIONS - pHScan - Pol2

Date	86-08-15	Pressure (MPa)	3
Tubes	25/46	Temperature (°C)	30
Salt	NaCl	Cfv (m/s)	4.5
Salt Conc (mg/l)	2920	Direction of Scan	4 --> 9

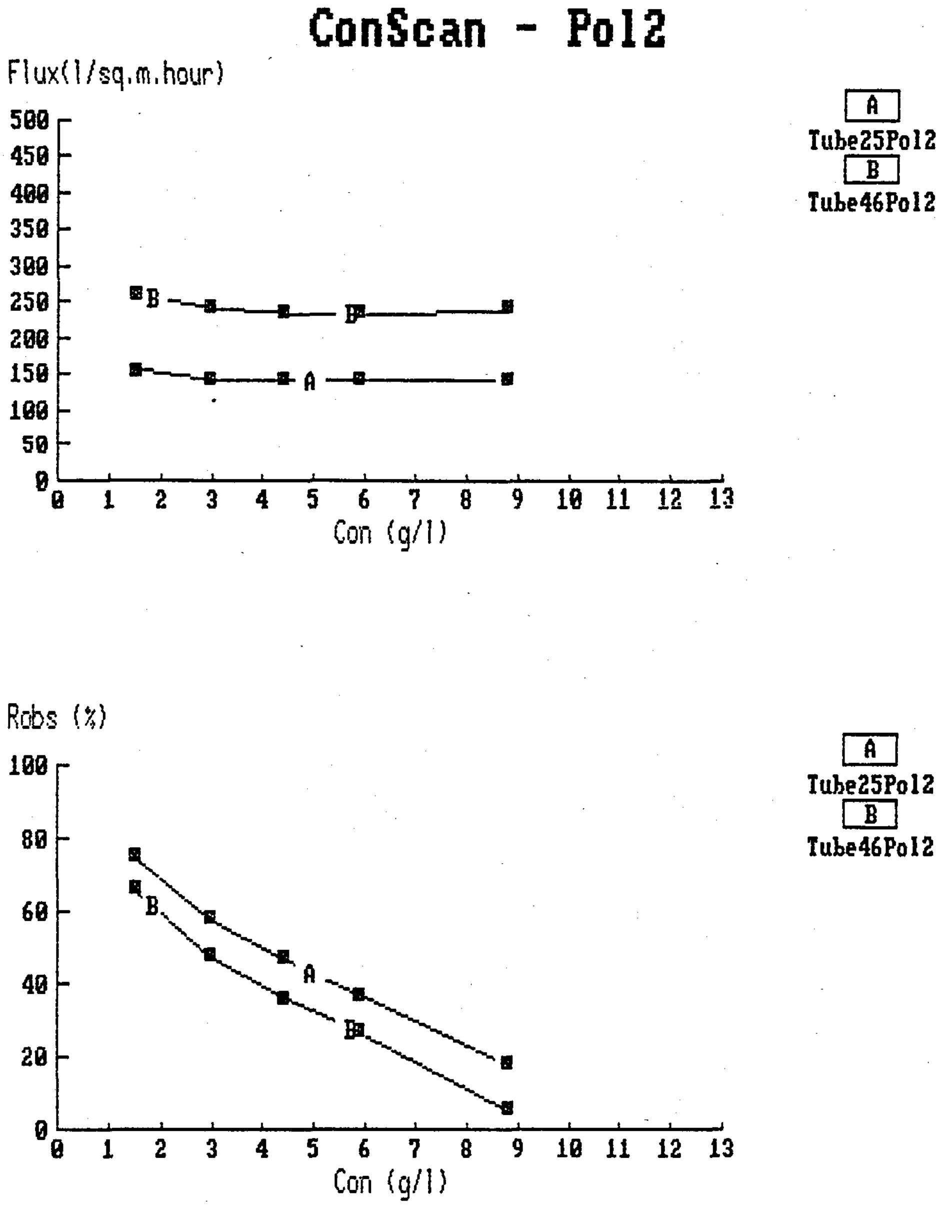


FIGURE 7: Performance vs Concentration during ConScan Pol2 Membrane

EXPERIMENTAL CONDITIONS - ConScan - Pol2

Date	86-08-14	Pressure (MPa)	3
Tubes	25/46	Temperature (°C)	30
Salt	NaCl	Cfv (m/s)	4.5
Salt Conc (g/l)	1 - 9	pH	7
Direction of Scan	1 —> 9		

TABLE 7 : Performance of Membranes at different Concentrations

Data for Figure 7 - Concentration Scan

Po12	Flux (l/sq.m.hour)		Robs (%)	
Con\Tube	25	46	25	46
1.46	153.42	258.62	74.55	65.91
2.92	140.27	241.08	57.73	47.42
4.38	140.27	232.32	46.79	35.90
5.84	140.27	232.32	36.67	26.67
8.76	140.27	241.08	17.72	5.06
2.92*	144.65	245.47	47.58	40.32

EXPERIMENTAL CONDITIONS - ConScan - Po12

Date	86-08-14	Pressure (MPa)	3
Tubes	25/46	Temperature (°C)	30
Salt	NaCl	Cfv (m/s)	4.5
Salt Conc (g/l)	1 - 9	pH	7
Direction of Scan	1 —> 9		

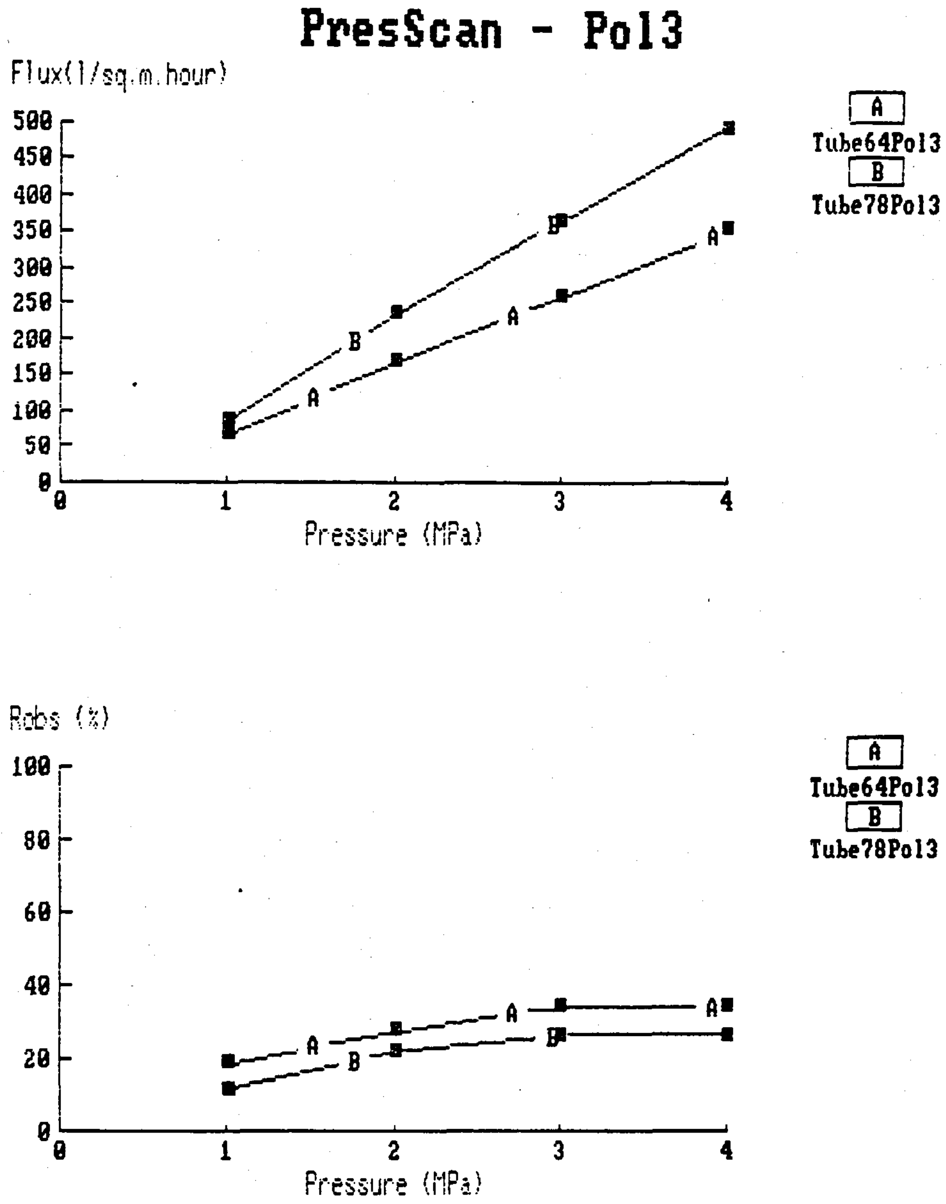


FIGURE 8: Performance vs Pressure during Pressure Scan Pol3 Membrane

EXPERIMENTAL CONDITIONS - PresScan - Pol3

Date	87-09-29	pH	7
Tubes	64/78	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 —> 4

TABLE 8: Performance of Membranes at Different Pressures

Data for Figure 8 - Pressure Scan - Pol3

Pol3	Flux (l/sq.m.hour)		Robs (%)	
Pres\Tube	64	78	64	78
3*	258.62	368.20	34.48	26.44
1	65.75	85.48	18.39	11.49
2	166.57	232.32	27.59	21.84
3	258.62	363.82	34.09	26.14
4	350.67	490.93	34.09	26.14
3*	258.62	363.82	32.95	25

EXPERIMENTAL CONDITIONS - PresScan - Pol3

Date	87-09-29	pH	7
Tubes	64/78	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 --> 4

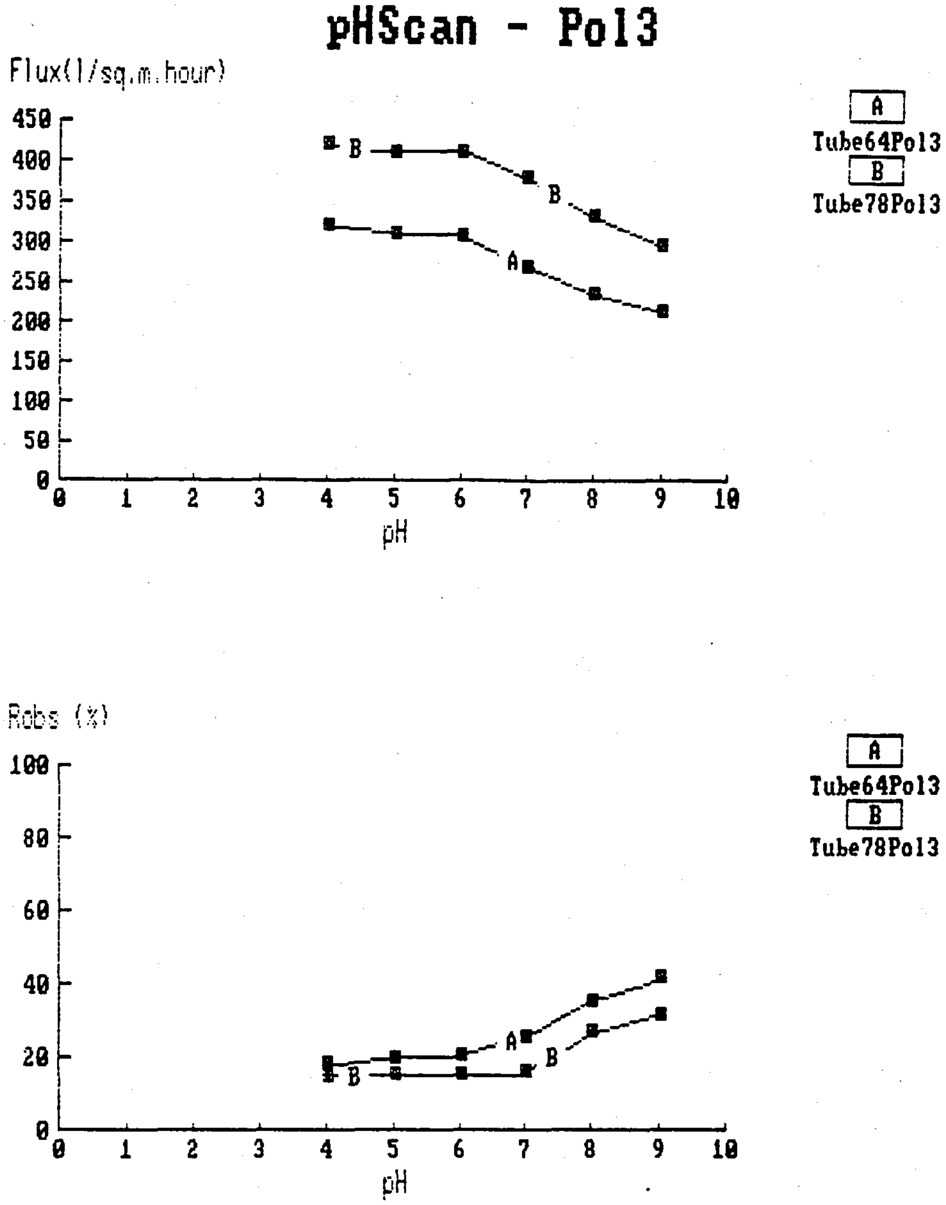


FIGURE 9: Performance vs pH during pH Scan
Pol3 Membrane

EXPERIMENTAL CONDITIONS - pHScan - 8703

Date	87-10-02	Pressure (MPa)	3
Tubes	64/78	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 —> 9

TABLE 9: Performance of Membranes at different pH

Data for Figure 9 - pH Scan - Pol3

Pol3	Flux (l/sq.m.hour)		Robs (%)	
pH\Tube	64	78	64	78
7*	254.23	355.05	30.68	23.86
4	315.60	416.42	17.78	14.44
5	306.83	407.65	19.55	14.61
6	302.45	407.65	20.22	14.61
7	267.38	376.97	25.56	15.56
8	232.32	328.75	35.16	26.37
9	210.40	293.68	41.30	31.52
7*	241.08	324.37	34.07	26.37

EXPERIMENTAL CONDITIONS - pHScan - 8703

Date	87-10-02	Pressure (MPa)	3
Tubes	64/78	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 --> 9

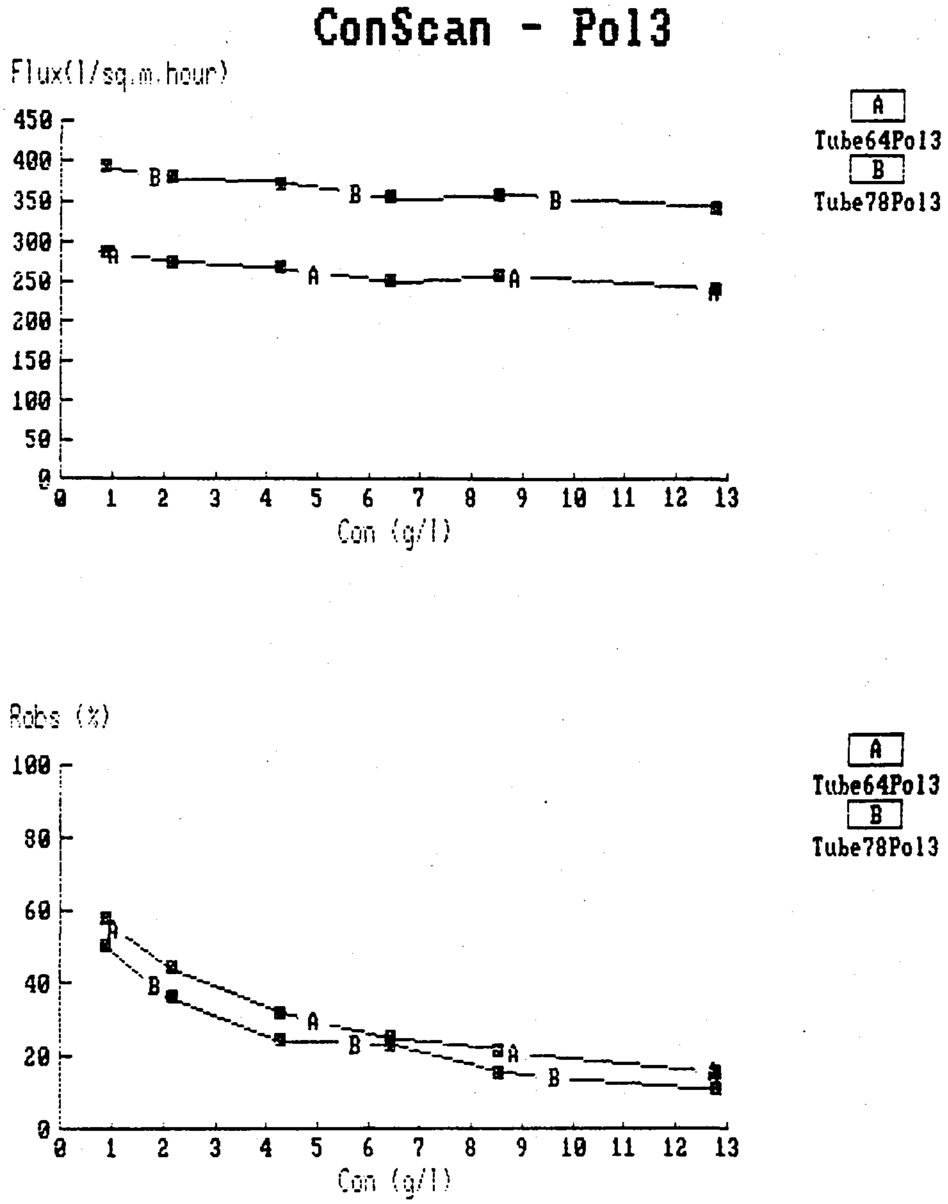


FIGURE 10: Performance vs Concentration during Con Scan Pol3 Membrane

EXPERIMENTAL CONDITIONS - ConScan - 8703

Date	87-10-01	Pressure (MPa)	3
Tubes	64/78	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 ---> 13		

TABLE 10: Performance of Membranes at Different Concentrations

Data for Figure 10 - Concentration Scan - Pol3

Pol3	Flux (l/sq.m.hour)		Robs (%)	
Con\Tube	64	78	64	78
0.85	284.92	390.12	56.86	50
2.13	271.77	376.97	43.75	35.42
4.25	263.00	368.20	31.36	23.86
6.37	245.47	350.67	24.62	22.62
8.50	254.23	355.05	20.93	15.12
12.75	236.70	337.52	15.20	10.40
4.25*	254.23	223.55	31.49	75.86

EXPERIMENTAL CONDITIONS - ConScan - 8703

Date	87-10-01	Pressure (MPa)	3
Tubes	64/78	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 —> 13		

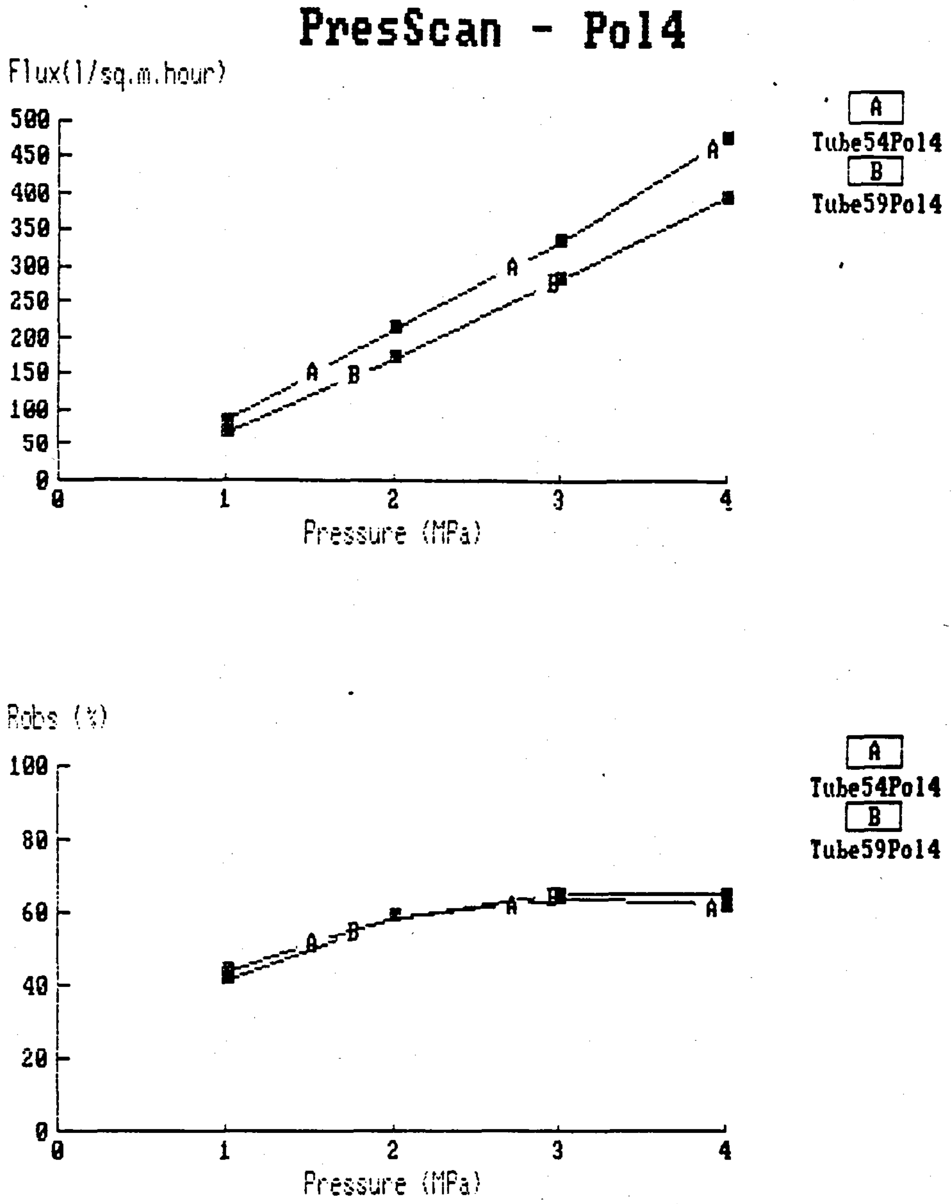


FIGURE 11: Performance vs Pressure during Pressure Scan Pol4 Membrane

EXPERIMENTAL CONDITIONS - PresScan - Pol4

Date	87-09-29	pH	7
Tubes	54/59	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 —> 4

TABLE 11: Performance of Membranes at Different Pressures

Data for Figure 11 - Pressure Scan - Po14

Po14	Flux (1/sq.m.hour)		Robs (%)	
Pres\Tube	54	59	54	59
3*	333.13	280.53	64.37	65.52
1	83.28	65.75	43.68	41.38
2	210.40	170.95	58.62	58.62
3	333.13	280.53	63.64	64.77
4	473.40	394.50	61.36	64.77
3*	333.13	280.53	63.50	63.64

EXPERIMENTAL CONDITIONS - PresScan - Po14

Date	87-09-29	pH	7
Tubes	54/59	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 --> 4

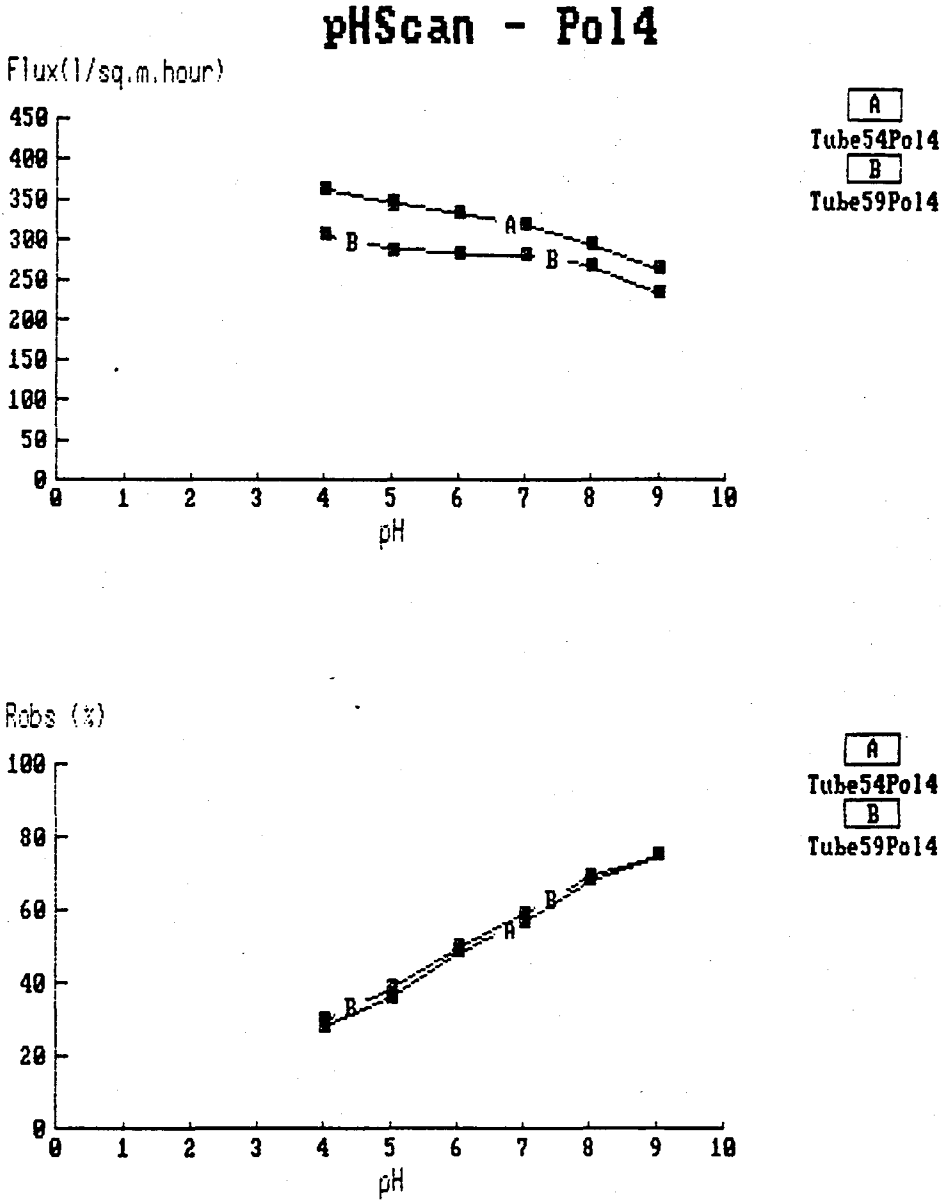


FIGURE 12: Performance vs pH during pH Scan
Pol4 Membrane

EXPERIMENTAL CONDITIONS – pH Scan – 8703

Date	87-10-02	Pressure (MPa)	3
Tubes	54/59	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 —> 9

TABLE 12: Performance of Membranes at different pH

Data for Figure 12 - pH Scan - Pol4

Pol4	Flux (l/sq.m.hour)		Robs (%)	
pH\Tube	54	59	54	59
7*	328.75	276.15	58.64	60.23
4	359.43	302.45	27.78	30
5	341.90	284.92	35.96	38.20
6	328.75	280.53	48.31	49.44
7	315.60	280.53	56.67	58.89
8	293.68	267.38	68.13	69.23
9	263.00	232.32	75	75
7*	311.22	280.53	60.44	61.54

EXPERIMENTAL CONDITIONS - pH Scan - 8703

Date	87-10-02	Pressure (MPa)	3
Tubes	54/59	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 —> 9

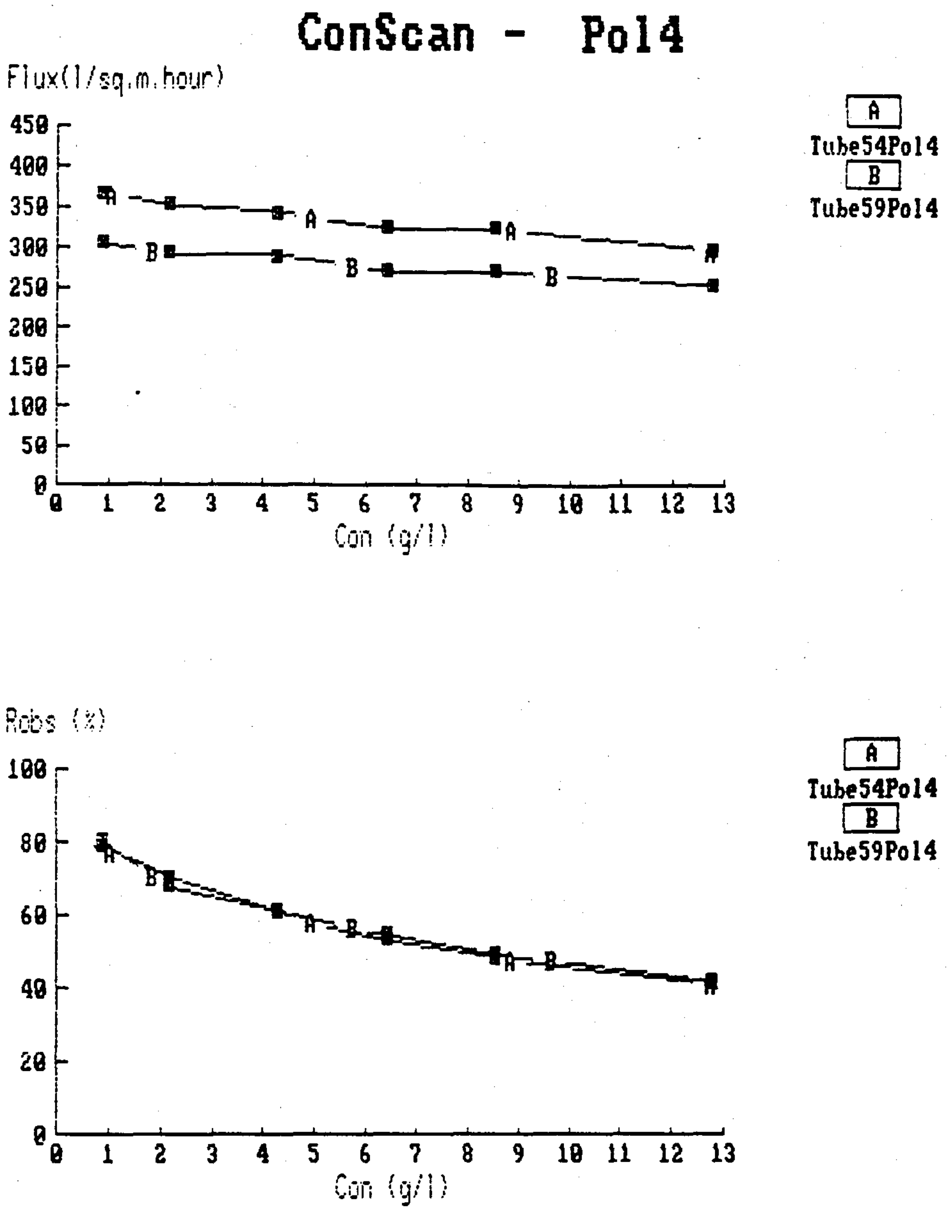


FIGURE 13: Performance vs Concentration during Con Scan Pol4 Membrane

EXPERIMENTAL CONDITIONS - ConScan - 8703

Date	87-10-01	Pressure (MPa)	3
Tubes	54/59	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 —> 13		

TABLE 13: Performance of Membranes at Different Concentrations

Data for Figure 13 - Concentration Scan - Pol4

Pol4	Flux (l/sq.m.hour)		Robs (%)	
Con\Tube	54	59	54	59
0.85	363.82	302.45	78.43	79.90
2.13	350.67	289.30	70	67.50
4.25	337.52	284.92	60.23	60.68
6.37	319.98	267.38	52.31	53.85
8.50	319.98	267.38	47.67	48.84
12.75	293.68	249.85	40.80	41.60
4.25*	328.75	276.15	59.77	60.92

EXPERIMENTAL CONDITIONS - ConScan - 8703

Date	87-10-01	Pressure (MPa)	3
Tubes	54/59	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 --> 13		

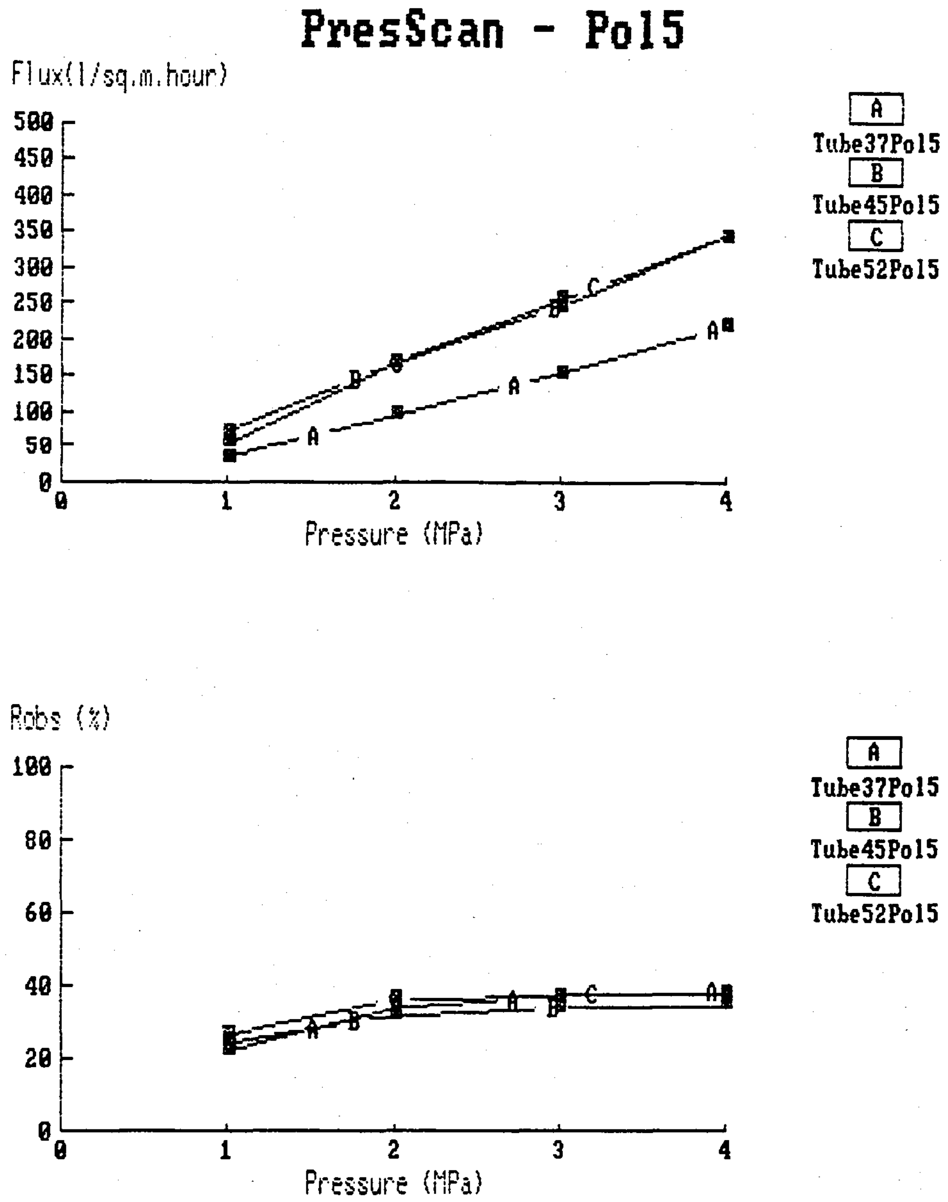


FIGURE 14: Performance vs Pressure during Pressure Scan
Po15 Membrane

EXPERIMENTAL CONDITIONS - PresScan - Po15

Date	88-04-07	pH	7
Tubes	37/45/53	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 —> 4

TABLE 14: Performance of Membranes at Different Pressures

Data for Figure 14 - Pressure Scan - Po15

Po15	Flux (l/sq.m.hour)			Robs (%)		
Pres\Tube	37	45	52	37	45	52
3*	153.42	258.62	258.62	37.78	33.33	36.67
1	35.07	72.33	54.79	21.98	24.18	26.37
2	96.43	166.57	166.57	34.07	31.87	36.26
3	153.42	245.47	254.23	37.36	34.07	37.36
4	219.17	341.90	341.90	38.04	34.78	38.04
3*	149.03	236.70	249.85	38.71	34.41	38.71

EXPERIMENTAL CONDITIONS - PresScan - Po15

Date	88-04-07	pH	7
Tubes	37/45/53	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 —> 4

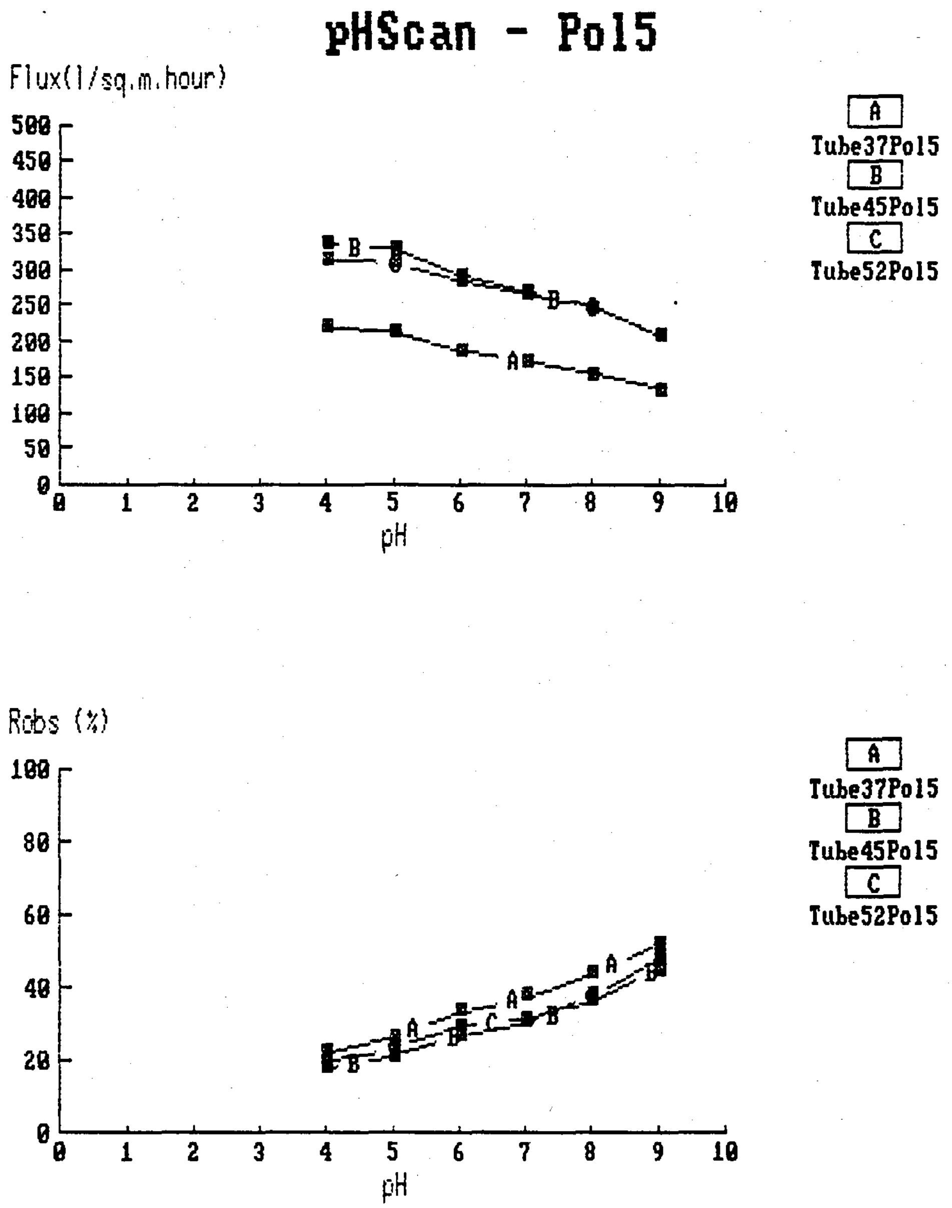


FIGURE 15: Performance vs pH during pH Scan
Pol5 Membrane

EXPERIMENTAL CONDITIONS - pH Scan - Pol5

Date	88-04-20	Pressure (MPa)	3
Tubes	37/45/52	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 —> 9

TABLE 15: Performance of Membranes at different pH

Data for Figure 15 - pH Scan - Po15

Po15	Flux (1/sq.m.hour)			Robs (%)		
pH\Tube	37	45	52	37	45	52
7*	175.33	271.77	267.38	36.17	28.72	29.79
4	219.17	333.13	311.22	22.11	17.89	20
5	210.40	324.37	306.83	26.32	21.05	23.16
6	184.10	289.30	280.53	33.33	27.08	29.17
7	170.95	267.38	263.00	37.50	30.21	31.25
8	153.42	245.47	245.47	43.75	36.46	37.50
9	131.50	206.02	206.02	52.08	44.79	47.92
7*	153.42	223.55	227.93	43.75	36.46	38.54

EXPERIMENTAL CONDITIONS - pH Scan - Po15

Date	88-04-20	Pressure (MPa)	3
Tubes	37/45/52	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 —> 9

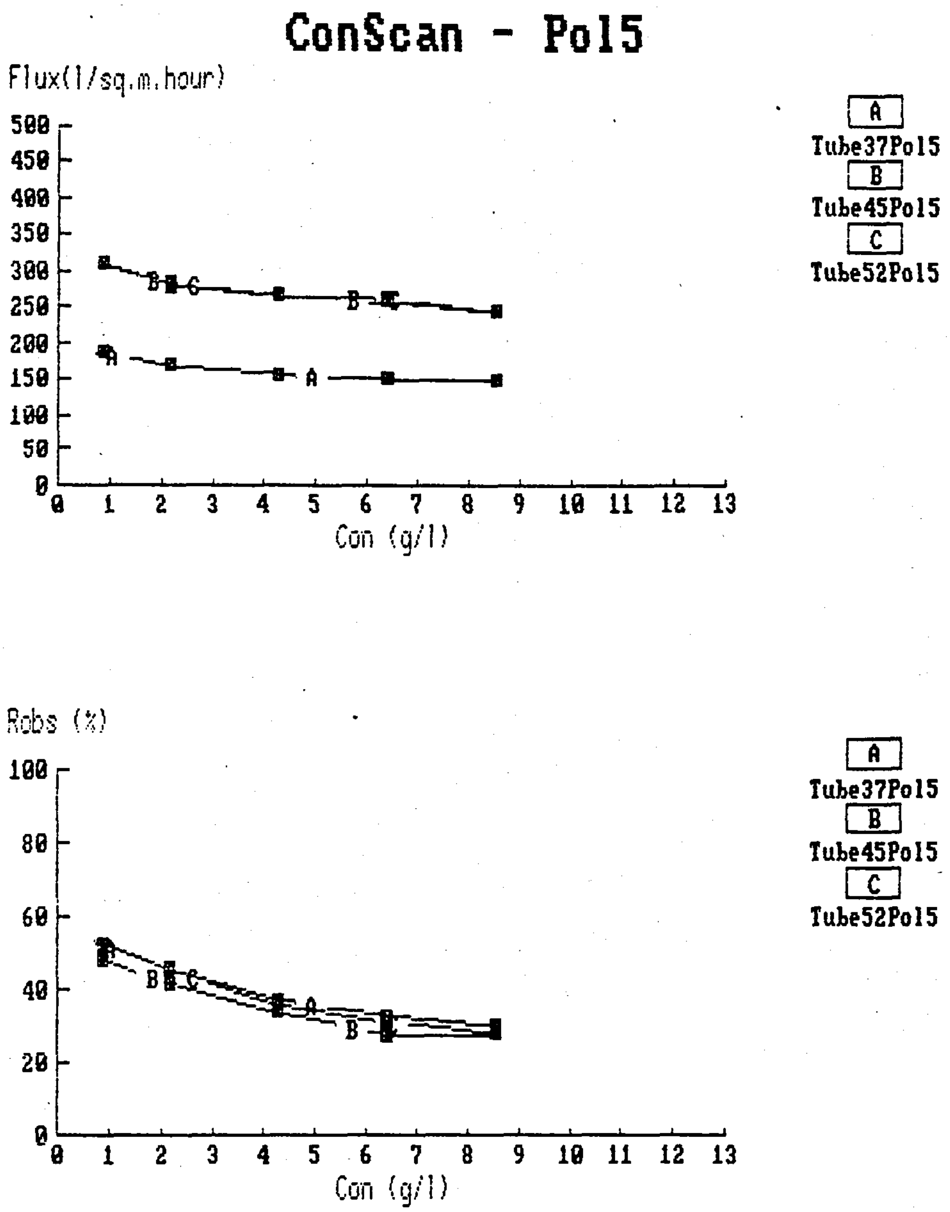


FIGURE 16: Performance vs Concentration during ConScan Pol5 Membrane

EXPERIMENTAL CONDITIONS - ConScan - Pol5

Date	88-04-14	Pressure (MPa)	3
Tubes	37/45/52	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 —> 13		

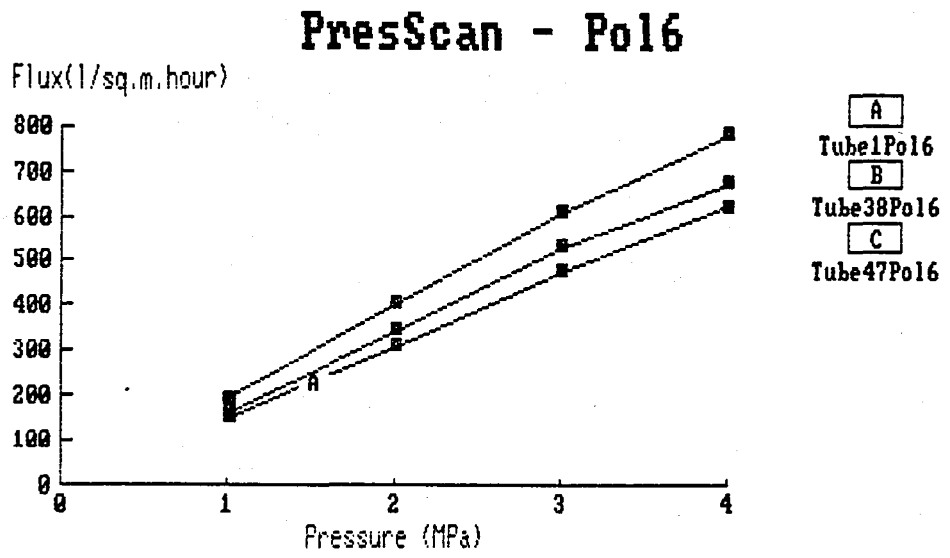
TABLE 16: Performance of Membranes at Different Concentrations

Data for Figure 16 - Concentration Scan

Po15	Flux (l/sq.m.hour)			Robs (%)		
Con\Tube	37	45	52	37	45	52
0.85	184.10	306.83	306.83	52.17	47.83	52.17
2.13	166.57	276.15	280.53	45.10	41.18	45.10
4.25	153.42	263.00	263.00	36.56	33.33	35.48
6.37	149.03	254.23	258.62	32.09	26.87	30.60
8.50	144.65	241.08	241.08	29.55	27.27	27.27

EXPERIMENTAL CONDITIONS - ConScan - Po15

Date	88-04-14	Pressure (MPa)	3
Tubes	37/45/52	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 —> 13		



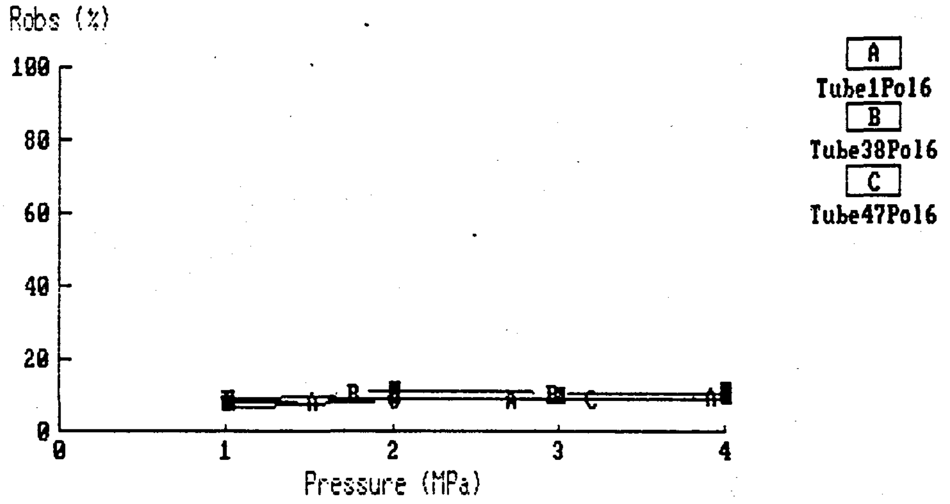


FIGURE 17: Performance vs Pressure during Pressure Scan Po16 Membrane

EXPERIMENTAL CONDITIONS - PresScan - Po16

Date	88-04-07	pH	7
Tubes	1/38/47	Temperature (°C)	30
Salt	$NaNO_3$	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 —> 4

TABLE 17:Performance of Membranes at Different Pressures

Data for Figure 17 - Pressure Scan - Po16

Po16	Flux (l/sq.m.hour)			Robs (%)		
Pres\Tube	1	38	47	1	38	47
3*	473.40	552.30	622.43	7.78	10	8.89
1	149.03	157.80	192.87	7.69	8.79	6.59
2	306.83	341.90	403.27	8.79	10.99	8.79
3	473.40	526.00	604.90	8.79	9.89	8.79
4	618.05	670.65	775.85	9.78	10.87	8.70
3*	447.10	490.93	578.60	9.68	11.83	9.68

EXPERIMENTAL CONDITIONS - PresScan - Po16

Date	88-04-07	pH	7
Tubes	1/38/47	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 —> 4

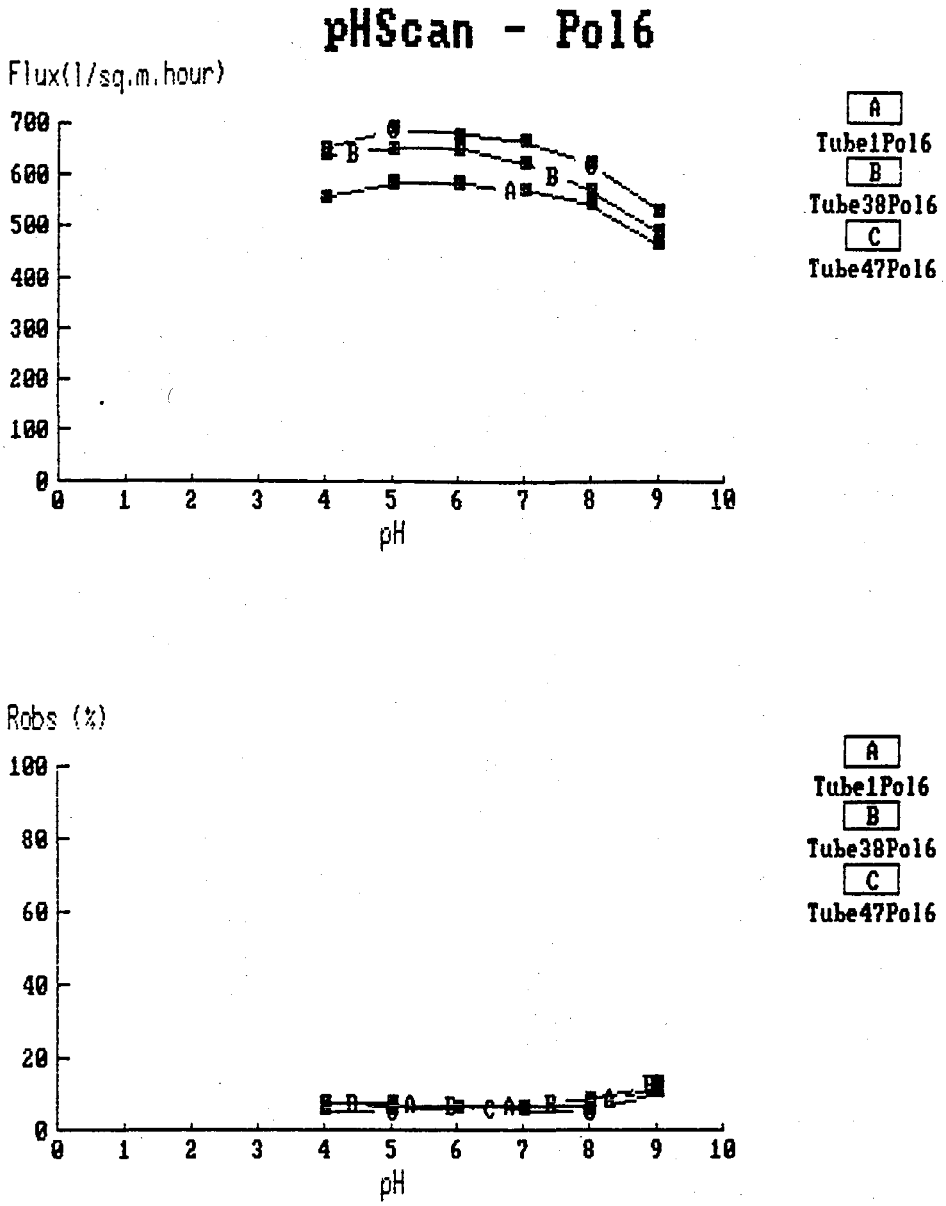


FIGURE 18: Performance vs pH during pH Scan
Po16 Membrane

EXPERIMENTAL CONDITIONS - pH Scan - Po16

Date	88-04-20	Pressure (MPa)	3
Tubes	1/38/47	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 —> 9

TABLE 18:Performance of Membranes at different pH

Data for Figure 18 - pH Scan - Po16

Po16	Flux (l/sq.m.hour)			Robs (%)		
pH\Tube	1	38	47	1	38	47
7*	539.15	604.90	644.35	6.38	6.38	4.26
4	552.30	631.20	644.35	7.37	7.37	5.26
5	578.60	644.35	683.80	7.37	6.32	5.26
6	578.60	644.35	670.65	6.25	6.25	6.25
7	565.45	618.05	657.50	6.25	6.25	5.21
8	539.15	565.45	618.05	7.29	8.33	5.21
9	460.25	486.55	526.00	11.46	12.50	10.42
7*	469.02	499.70	526.00	9.38	9.38	6.25

EXPERIMENTAL CONDITIONS - pH Scan - Po16

Date	88-04-20	Pressure (MPa)	3
Tubes	1/38/47	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 —> 9

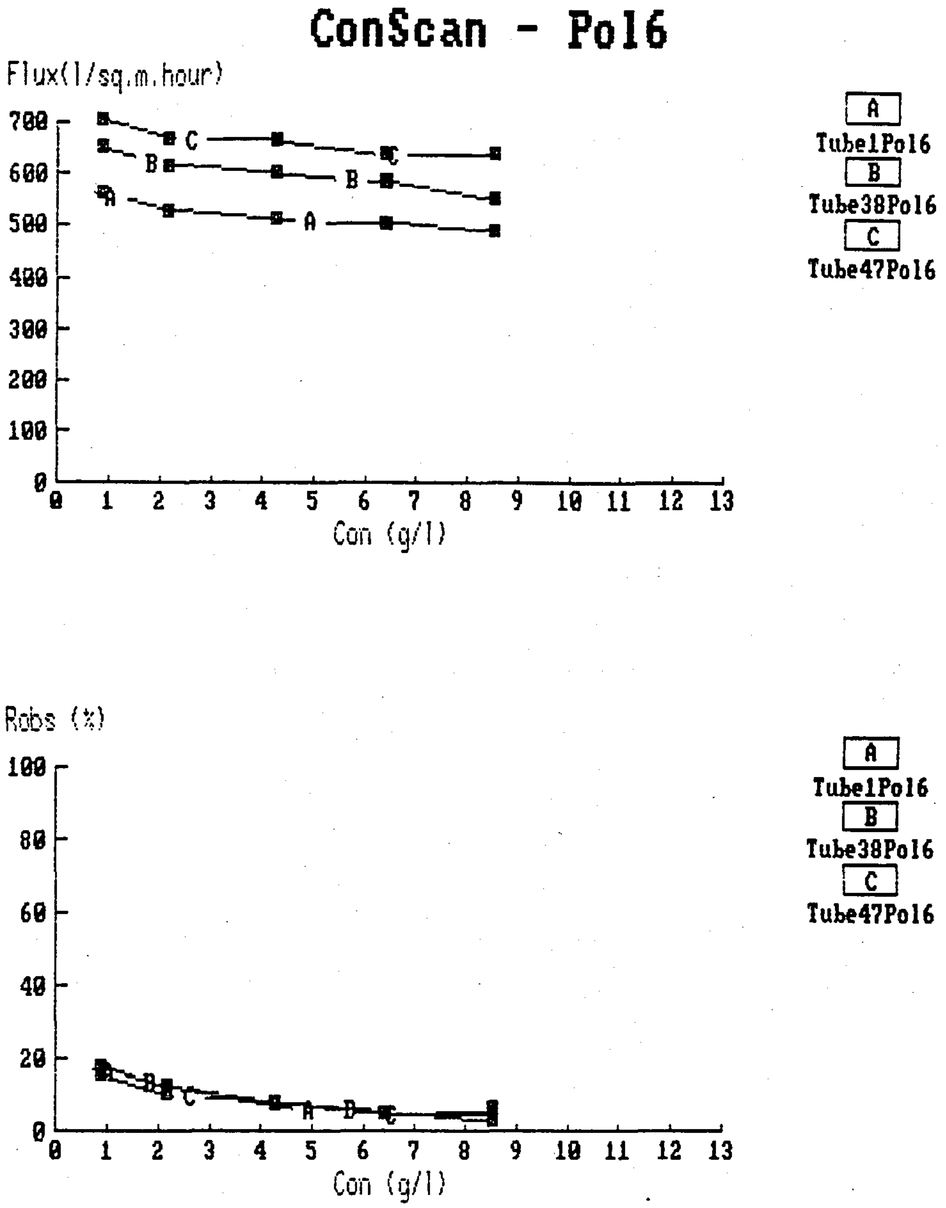


FIGURE 19: Performance vs Concentration during ConScan Po16 Membrane

EXPERIMENTAL CONDITIONS - ConScan - Po16

Date	88-04-14	Pressure (MPa)	3
Tubes	1/38/47	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 —> 13		

TABLE 19: Performance of Membranes at Different Concentrations

Data for Figure 19 - Concentration Scan

Po16	Flux (l/sq.m.hour)			Robs (%)		
Con\Tube	1	38	47	1	38	47
0.85	561.07	648.73	701.33	16.52	17.39	14.78
2.13	526.00	613.67	666.27	11.76	11.76	9.80
4.25	508.47	596.13	657.50	6.45	7.53	7.53
6.37	499.70	578.60	631.20	4.48	4.48	4.48
8.50	482.17	543.53	631.20	5.68	4.55	2.27

EXPERIMENTAL CONDITIONS - ConScan - Po16

Date	88-04-14	Pressure (MPa)	3
Tubes	1/38/47	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 —> 13		

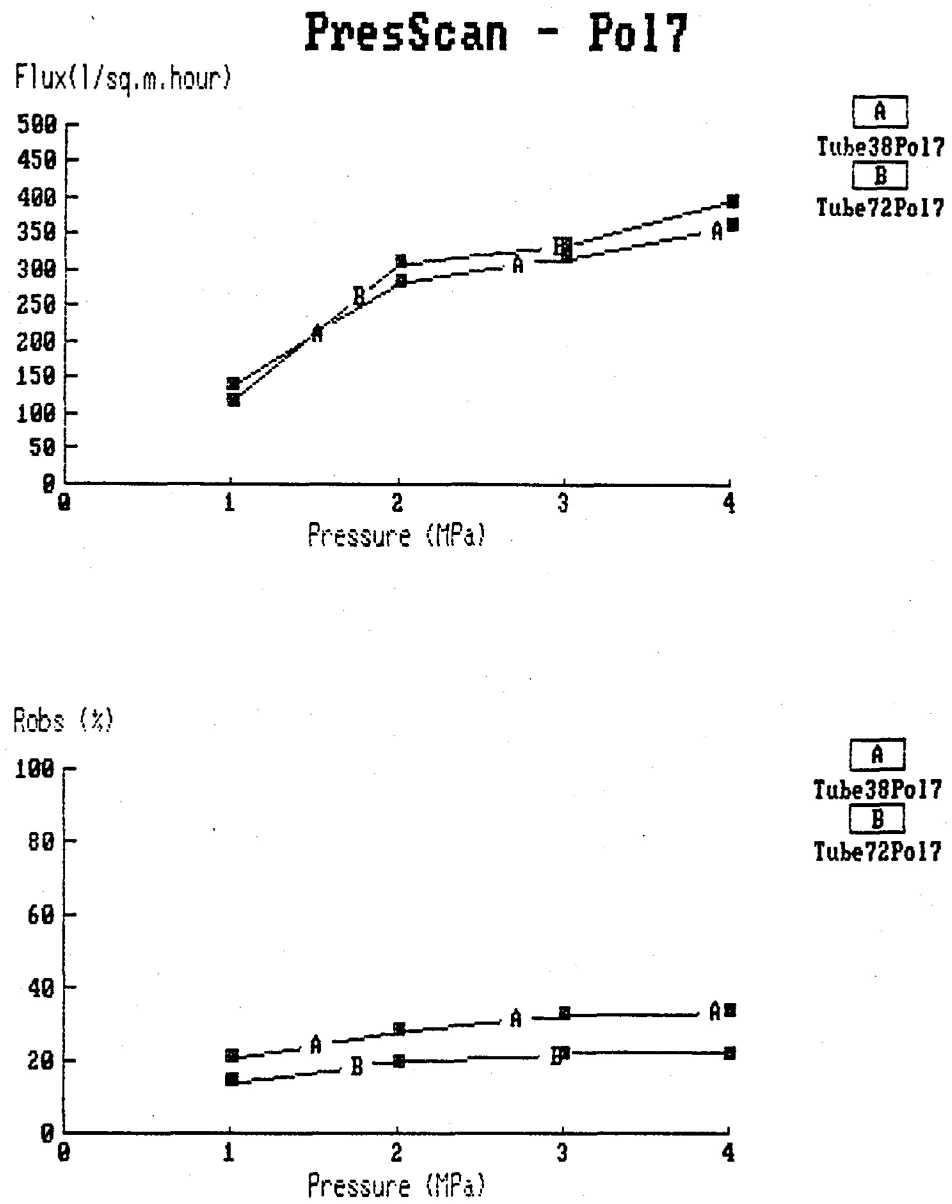


FIGURE 20: Performance vs Pressure during Pressure Scan Pol7 Membrane

EXPERIMENTAL CONDITIONS - PresScan - Pol7

Date	88-07-18	pH	7
Tubes	38/72	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 —> 4

TABLE 20: Performance of Membranes at Different Pressures

Data for Figure 20 - Pressure Scan - Pol7

Pol7	Flux (1/sq.m.hour)		Robs (%)	
Pres\Tube	38	72	38	72
3*	460.25	473.40	31.52	21.74
1	135.88	113.97	20.65	14.13
2	280.53	306.83	28.26	19.57
3	315.60	333.13	32.61	21.74
4	359.43	394.50	33.70	21.74
3*	280.53	306.83	31.52	22.83

EXPERIMENTAL CONDITIONS - PresScan - Pol7

Date	88-07-18	pH	7
Tubes	38/72	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 —> 4

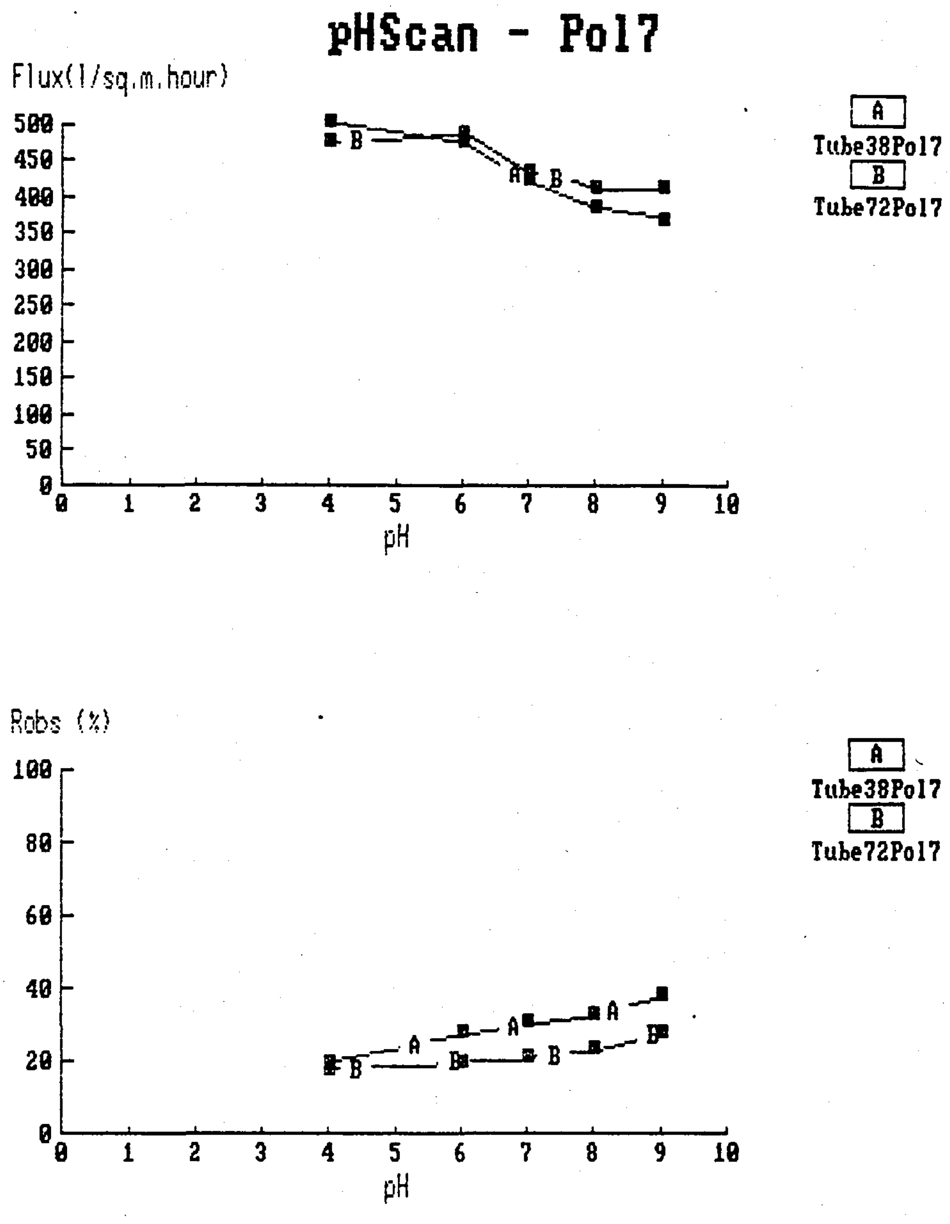


FIGURE 21: Performance vs pH during pH Scan
Pol7 Membrane

EXPERIMENTAL CONDITIONS - pH Scan - Pol7

Date	88-07-20	Pressure (MPa)	3
Tubes	38/72	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 —> 9

TABLE 21: Performance of Membranes at different pH

Data for Figure 21 - pH Scan - Po17

Po17	Flux (l/sq.m.hour)		Robs (%)	
pH\Tube	38	72	38	72
7*	447.10	460.25	29.35	20.65
4	499.70	473.40	19.57	17.39
6	473.40	486.55	27.17	19.57
7	420.80	433.95	30.43	20.65
8	385.73	412.03	32.61	22.83
9	368.20	412.03	37.89	27.37
7*	394.50	473.40	31.58	23.16

EXPERIMENTAL CONDITIONS - pH Scan - Po17

Date	88-07-20	Pressure (MPa)	3
Tubes	38/72	Temperature (°C)	30
Salt	$NaNO_3$	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 --> 9

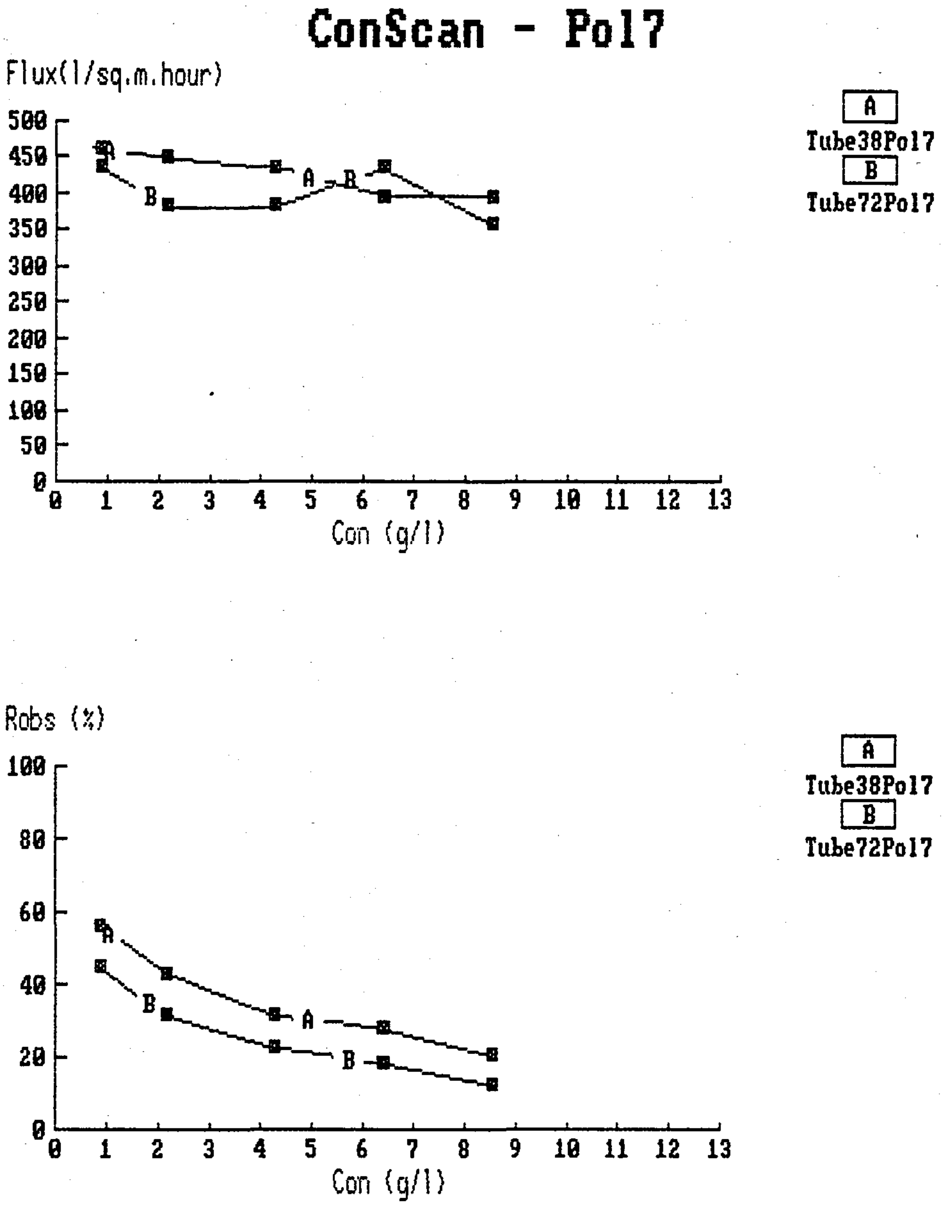


FIGURE 22: Performance vs Concentration during ConScan Pol7 Membrane

EXPERIMENTAL CONDITIONS - ConScan - Pol7

Date	88-07-19	Pressure (MPa)	3
Tubes	38/72	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 --> 13		

TABLE 22: Performance of Membranes at Different Concentrations

Data for Figure 22 - Concentration Scan - Po17

Po17	Flux (l/sq.m.hour)		Robs (%)	
Con\Tube	38	72	38	72
0.85	460.25	433.95	55.77	44.23
2.13	447.10	381.35	42.50	31.25
4.25	433.95	381.35	31.11	22.22
6.37	394.50	433.95	27.19	17.54
8.50	394.50	355.05	20	12

EXPERIMENTAL CONDITIONS - ConScan - Po17

Date	88-07-19	Pressure (MPa)	3
Tubes	38/72	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 —> 13		

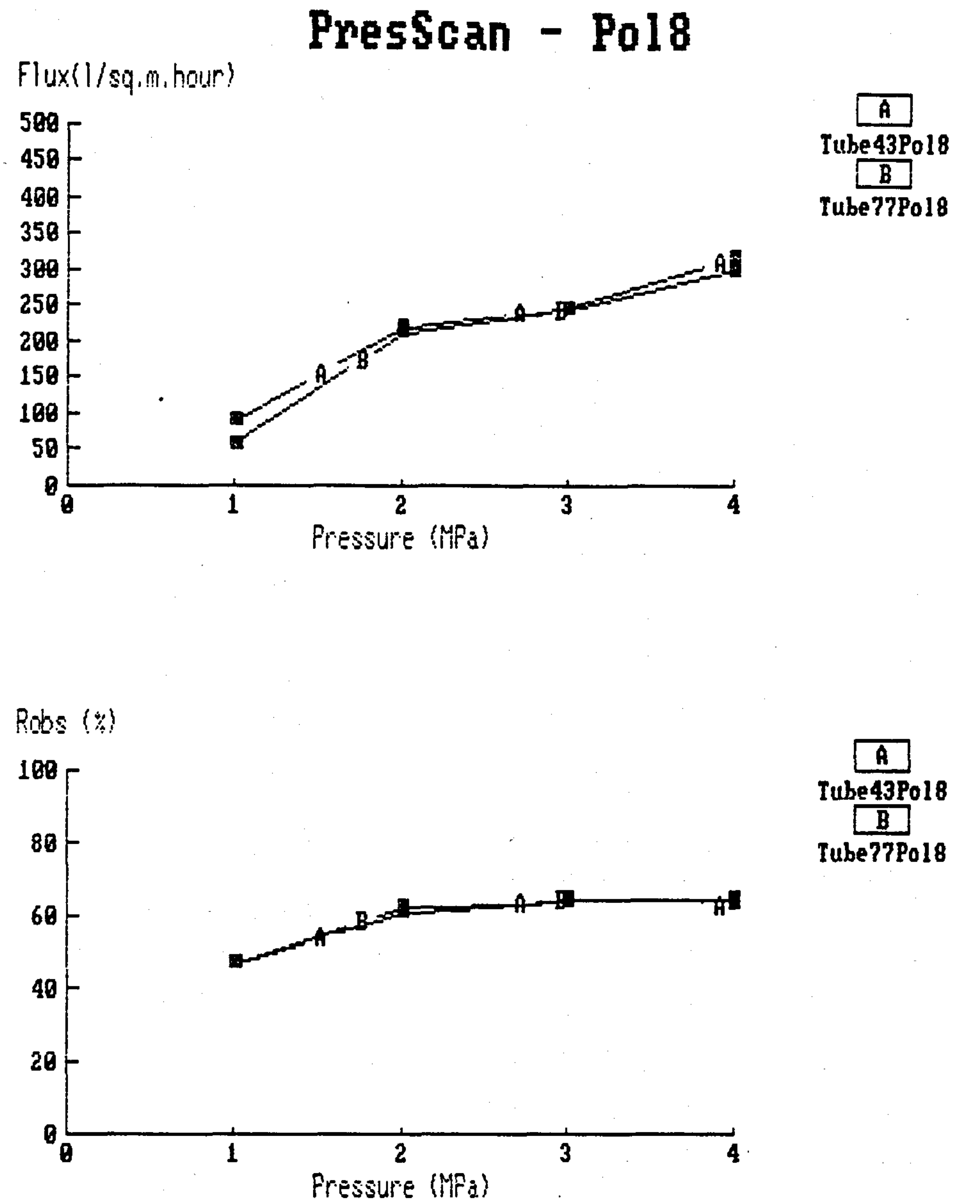


FIGURE 23: Performance vs Pressure during Pressure Scan
Po18 Membrane

EXPERIMENTAL CONDITIONS - PresScan - Po18

Date	88-07-18	pH	7
Tubes	43/77	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 —> 4

TABLE 23: Performance of Membranes at Different Pressures

Data for Figure 23 - Pressure Scan - Po18

Po18	Flux (l/sq.m.hour)		Robs (%)	
Pres\Tube	43	77	43	77
3*	355.05	355.05	65.22	66.30
1	87.67	56.98	46.74	46.74
2	219.17	210.40	60.87	61.96
3	245.47	245.47	64.13	64.13
4	315.60	298.07	63.04	64.13
3*	227.93	227.93	63.04	64.13

EXPERIMENTAL CONDITIONS - PresScan - Po18

Date	88-07-18	pH	7
Tubes	43/77	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 --> 4

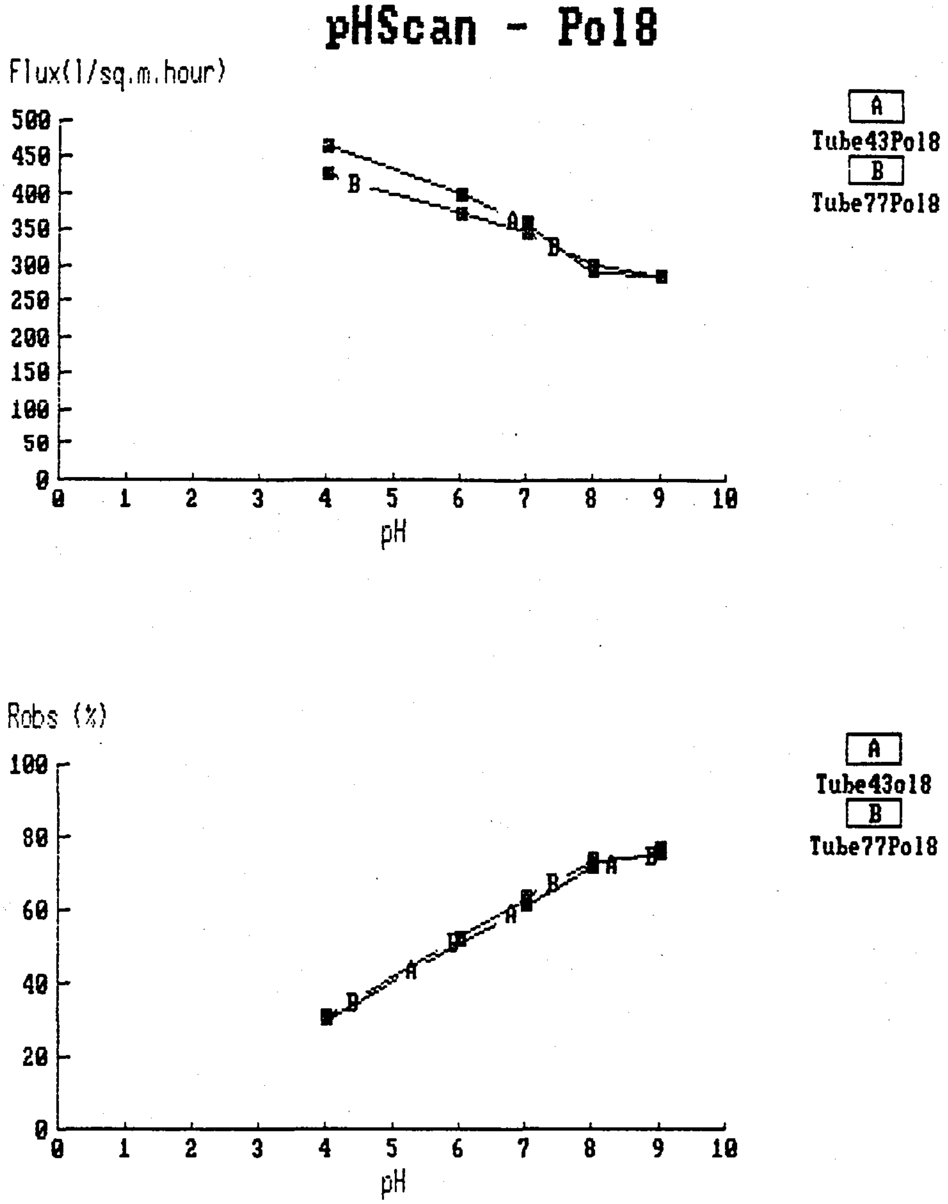


FIGURE 24: Performance vs pH during pH Scan
Po18 Membrane

EXPERIMENTAL CONDITIONS - pH Scan - Po18

Date	88-07-20	Pressure (MPa)	3
Tubes	43/77	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 —> 9

TABLE 24: Performance of Membranes at different pH

Data for Figure 24 - pH Scan - Po18

Po18	Flux (l/sq.m.hour)		Robs (%)	
pH\Tube	43	77	43	77
7*	355.05	341.90	59.78	61.96
4	460.25	420.80	29.35	30.43
6	394.50	368.20	51.09	52.17
7	355.05	341.90	60.87	63.04
8	289.30	298.07	71.30	73.48
9	280.53	280.53	76	75.16
7*	333.13	324.37	61.05	61.05

EXPERIMENTAL CONDITIONS - pH Scan - Po18

Date	88-07-20	Pressure (MPa)	3
Tubes	43/77	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 —> 9

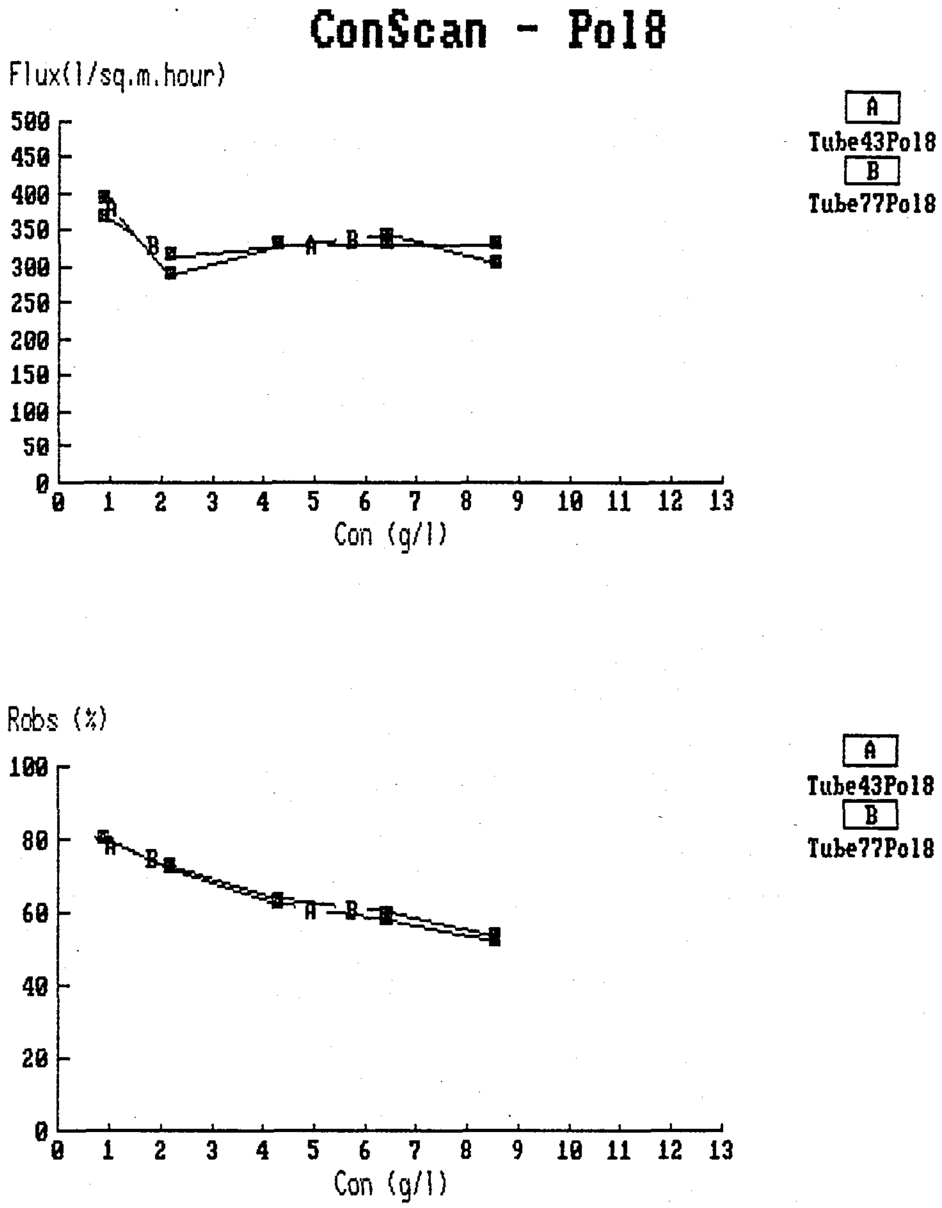


FIGURE 25: Performance vs Concentration during ConScan Pol8 Membrane

EXPERIMENTAL CONDITIONS - ConScan - Pol8

Date	88-07-19	Pressure (MPa)	3
Tubes	43/77	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 --> 13		

TABLE 25: Performance of Membranes at Different Concentrations

Data for Figure 25 - Concentration Scan - Po18

Po18	Flux (l/sq.m.hour)		Robs (%)	
Con\Tube	43	77	43	77
0.85	394.50	368.20	79.81	79.81
2.13	289.30	315.60	71.67	72.50
4.25	328.75	328.75	62.22	63.33
6.37	328.75	341.90	57.89	59.65
8.50	328.75	302.45	52	53.33

EXPERIMENTAL CONDITIONS - ConScan - Po18

Date	88-07-19	Pressure (MPa)	3
Tubes	43/77	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 —> 13		

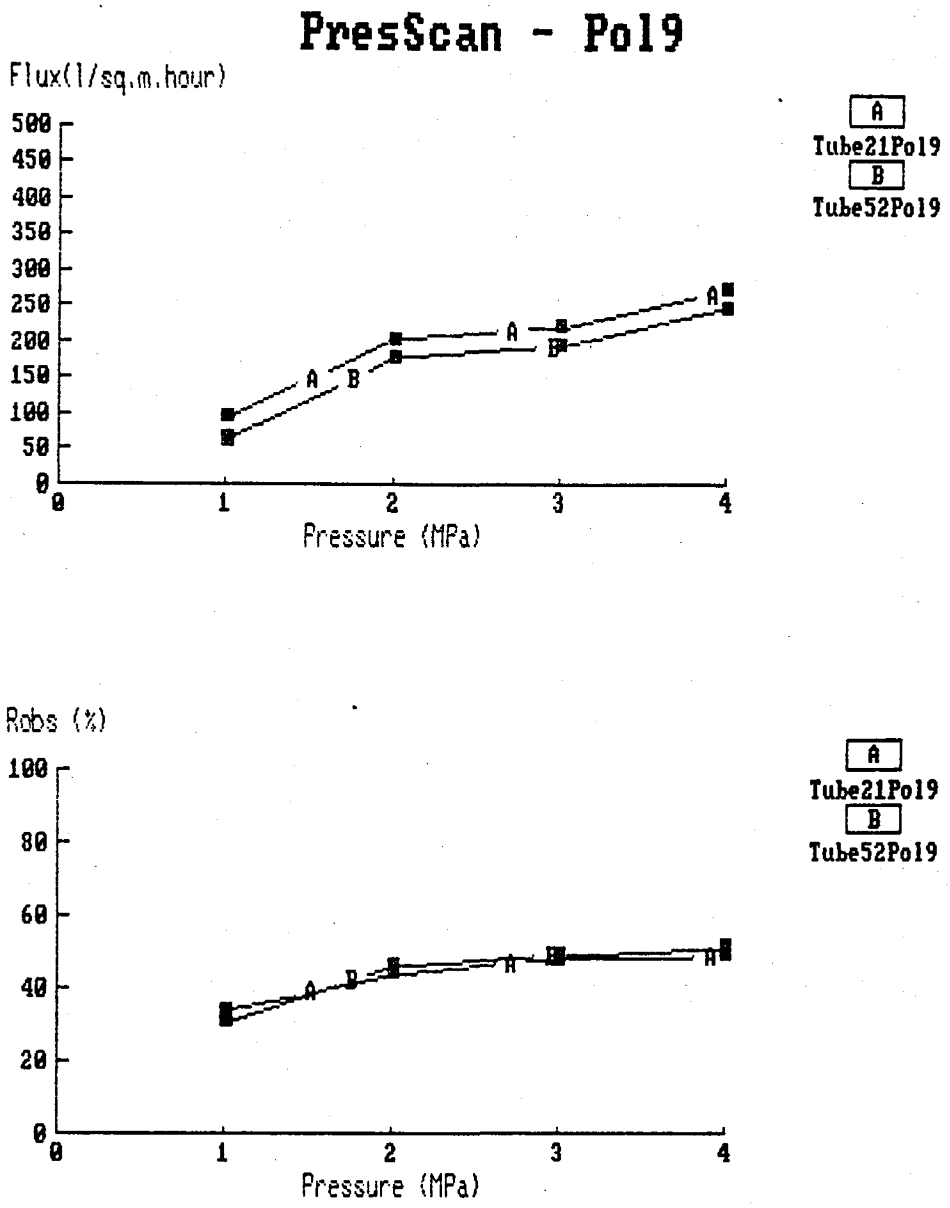


FIGURE 26: Performance vs Pressure during Pressure Scan Po19 Membrane

EXPERIMENTAL CONDITIONS - PresScan - Po19

Date	88-07-18	pH	7
Tubes	21/52	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 —> 4

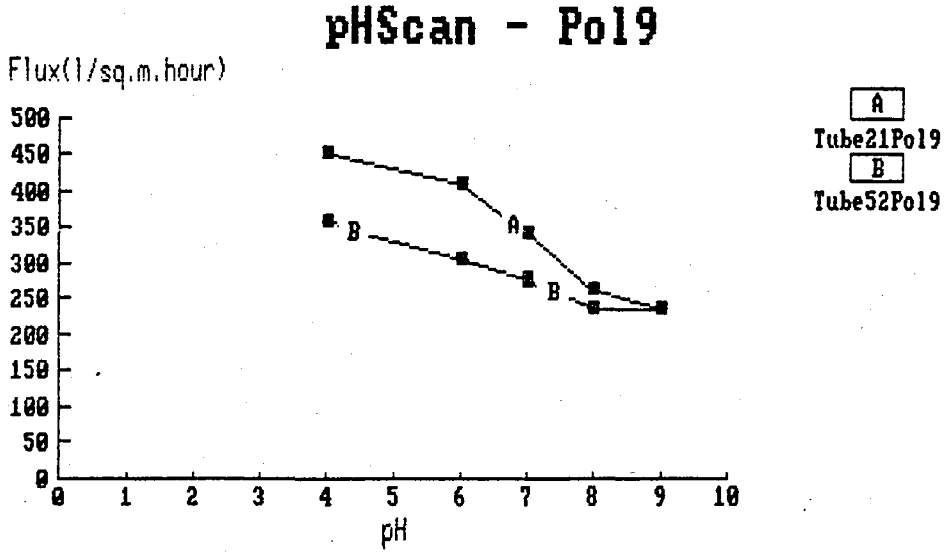
TABLE 26: Performance of Membranes at Different Pressures

Data for Figure 26 - Pressure Scan - Po19

Po19	Flux (l/sq.m.hour)		Robs (%)	
Pres\Tube	21	52	21	52
3*	315.60	276.15	48.91	51.09
1	92.05	61.37	33.70	30.43
2	201.63	175.33	43.48	45.65
3	219.17	192.87	47.83	48.91
4	271.77	245.47	48.91	51.09
3*	210.40	184.10	48.91	50

EXPERIMENTAL CONDITIONS - PresScan - Po19

Date	88-07-18	pH	7
Tubes	21/52	Temperature (°C)	30
Salt	$NaNO_3$	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 —> 4



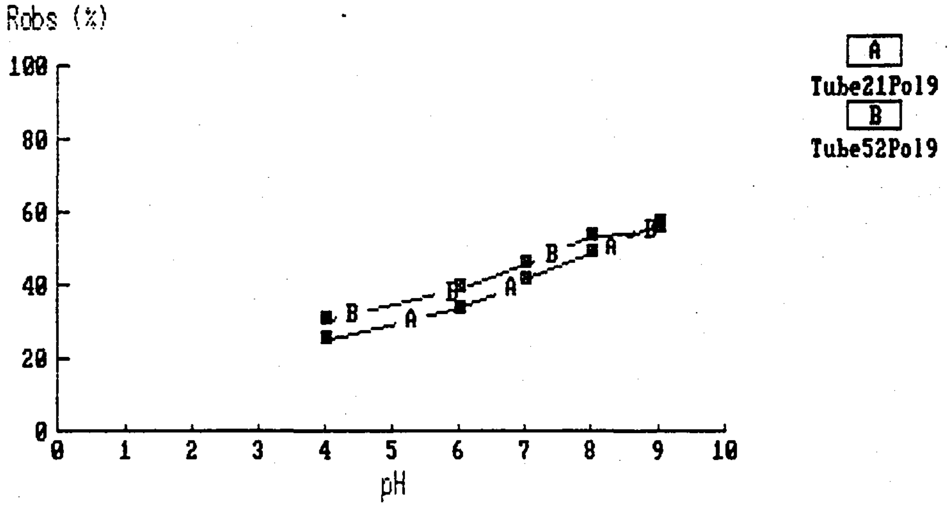


FIGURE 27: Performance vs pH during pH Scan
Po19 Membrane

EXPERIMENTAL CONDITIONS - pH Scan - Po19

Date	88-07-20	Pressure (MPa)	3
Tubes	21/52	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 —> 9

TABLE 27: Performance of Membranes at different pH

Data for Figure 27 - pH Scan - Po19

Po19	Flux (l/sq.m.hour)		Robs (%)	
pH\Tube	21	52	21	52
7*	328.75	289.30	43.48	46.74
4	447.10	355.05	25	30.43
6	407.65	302.45	33.70	39.13
7	341.90	276.15	41.30	45.65
8	263.00	236.70	48.91	53.26
9	236.70	236.70	56.84	55.79
7*	271.77	263.00	48.42	45.26

EXPERIMENTAL CONDITIONS - pH Scan - Po19

Date	88-07-20	Pressure (MPa)	3
Tubes	21/52	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 —> 9

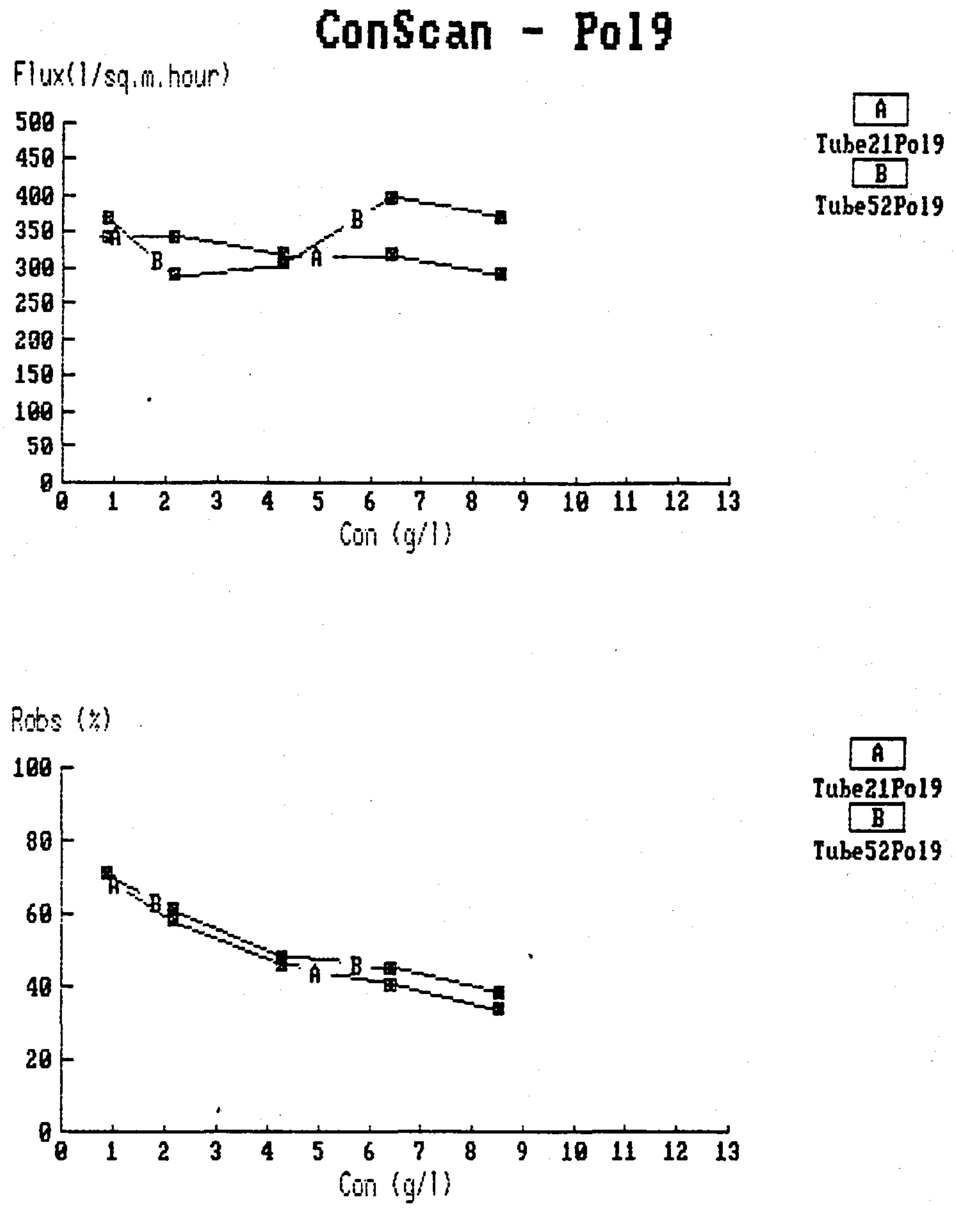


FIGURE 28: Performance vs Concentration during ConScan Po19 Membrane

EXPERIMENTAL CONDITIONS - ConScan - Po19

Date	88-07-19	Pressure (MPa)	3
Tubes	21/52	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 --> 13		

TABLE 28: Performance of Membranes at Different Concentrations

Data for Figure 28 - Concentration Scan

Pol9	Flux (1/sq.m.hour)		Robs (%)	
Con\Tube	21	52	21	52
0.85	341.90	368.20	70.19	70.19
2.13	341.90	289.30	57.50	60.83
4.25	315.60	302.45	45.56	47.78
6.37	315.60	394.50	40.35	44.74
8.50	289.30	368.20	33.33	38

EXPERIMENTAL CONDITIONS - ConScan - Pol9

Date	88-07-19	Pressure (MPa)	3
Tubes	21/52	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 --> 13		

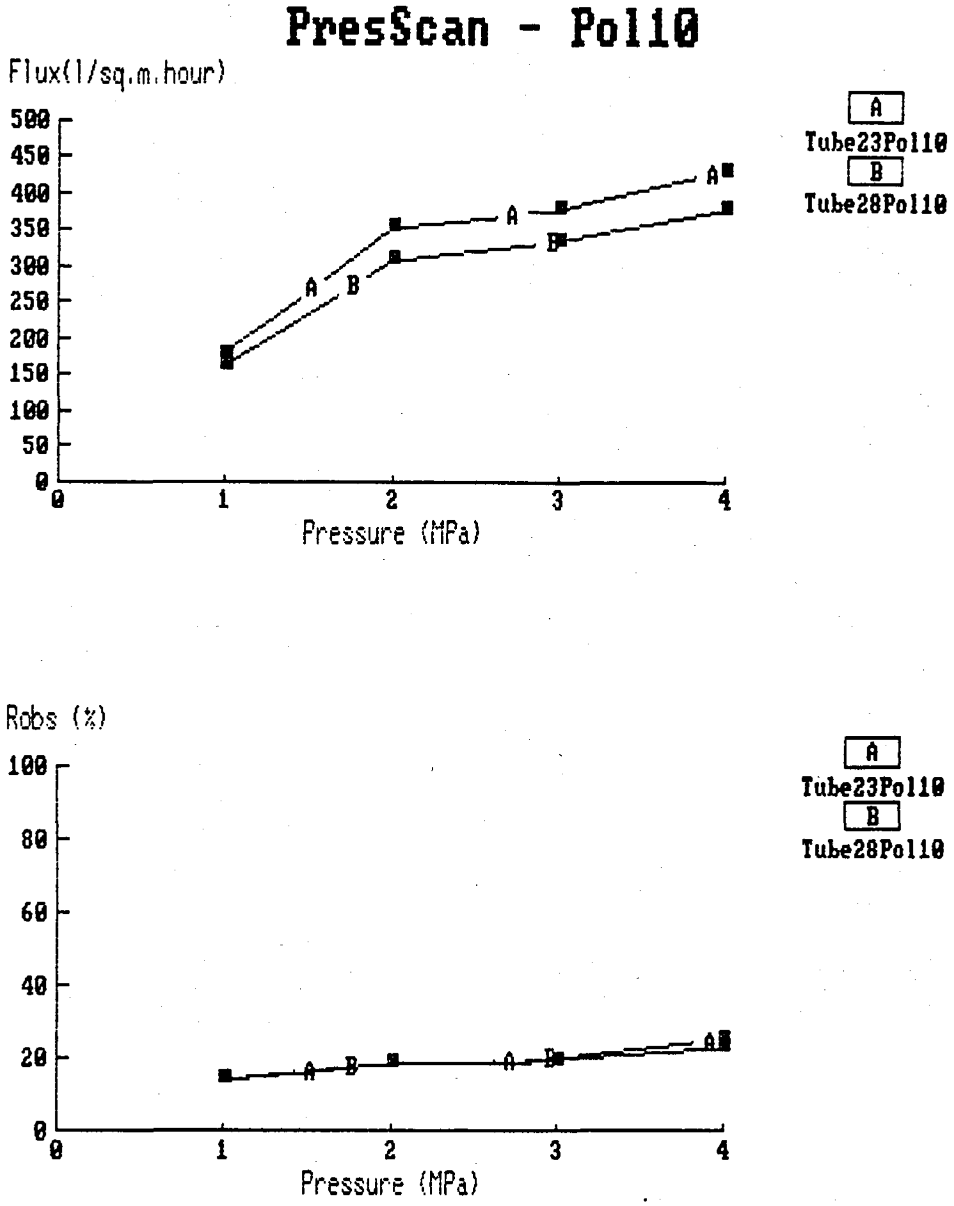


FIGURE 29: Performance vs Pressure during Pressure Scan Pol10 Membrane

EXPERIMENTAL CONDITIONS - PresScan - Pol10

Date	88-07-18	pH	7
Tubes	23/28	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 —> 4

TABLE 29: Performance of Membranes at Different Pressures

Data for Figure 29 - Pressure Scan - Pol10

Pol10	Flux (1/sq.m.hour)		Robs (%)	
Pres\Tube	23	28	23	28
3*	552.30	486.55	21.74	21.74
1	179.72	162.18	14.13	14.13
2	350.67	306.83	18.48	18.48
3	376.97	333.13	19.57	19.57
4	429.57	376.97	25	22.83
3*	333.13	289.30	23.91	21.74

EXPERIMENTAL CONDITIONS - PresScan - Pol10

Date	88-07-18	pH	7
Tubes	23/28	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	1 —> 4

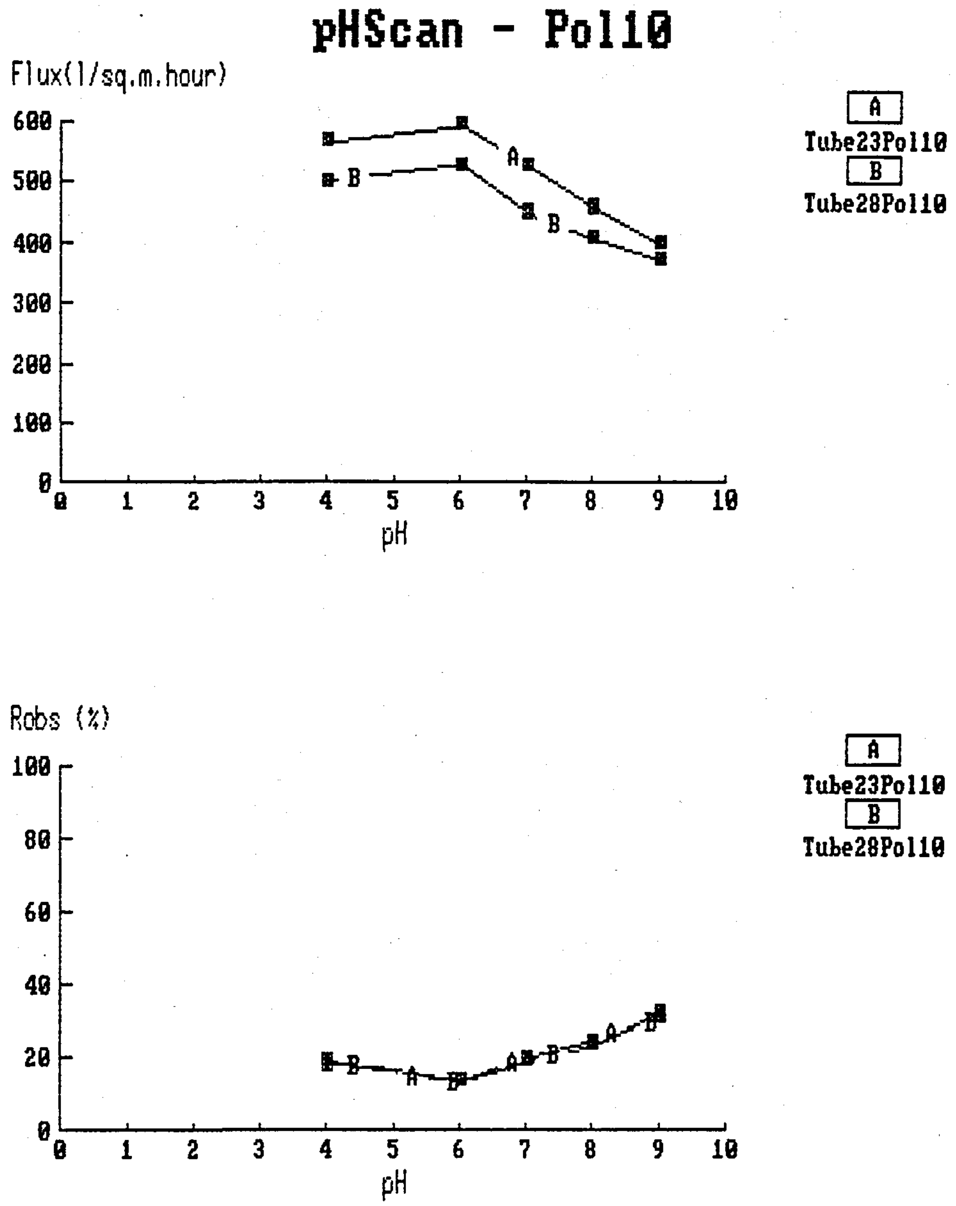


FIGURE 30: Performance vs pH during pH Scan
Pol10 Membrane

EXPERIMENTAL CONDITIONS - pH Scan - Pol10

Date	88-07-20	Pressure (MPa)	3
Tubes	23/28	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 —> 9

TABLE 30: Performance of Membranes at different pH

Data for Figure 30 - pH Scan - Pol10

Pol10	Flux (l/sq.m.hour)		Robs (%)	
pH\Tube	23	28	23	28
7*	473.40	433.95	22.83	21.74
4	565.45	499.70	17.39	18.48
6	591.75	526.00	13.04	13.04
7	526.00	447.10	19.57	18.48
8	455.87	403.27	23.91	22.83
9	394.50	368.20	31.58	30.53
7*	438.33	376.97	25.26	23.16

EXPERIMENTAL CONDITIONS - pH Scan - Pol10

Date	88-07-20	Pressure (MPa)	3
Tubes	23/28	Temperature (°C)	30
Salt	$NaNO_3$	Cfv (m/s)	4.5
Salt Conc (mg/l)	4249.5	Direction of Scan	4 --> 9

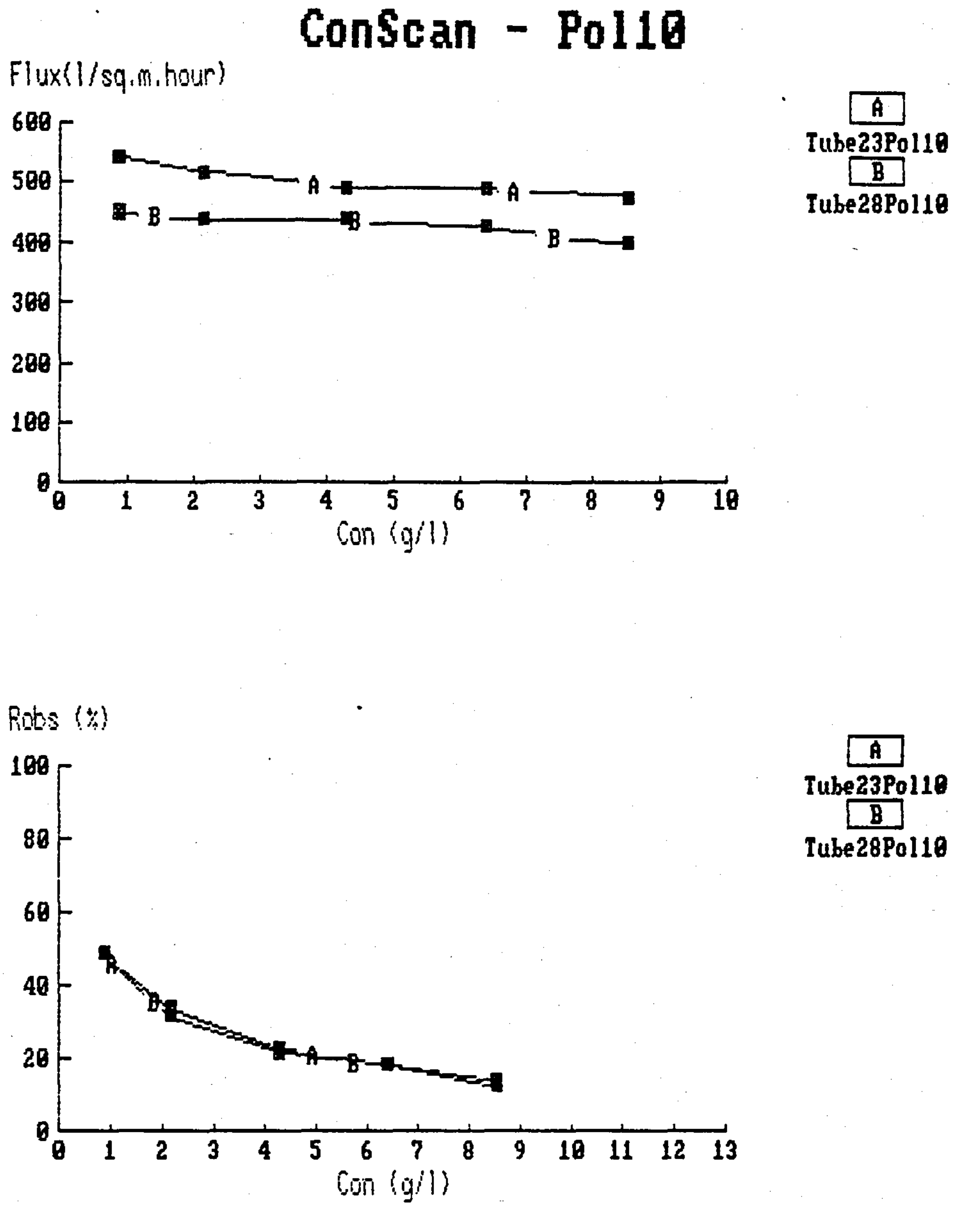


FIGURE 31: Performance vs Concentration during ConScan Pol10 Membrane

EXPERIMENTAL CONDITIONS - ConScan - Pol10

Date	88-07-19	Pressure (MPa)	3
Tubes	23/28	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/l)	0.8 - 13	pH	7
Direction of Scan	0.8 —> 13		

TABLE 31: Performance of Membranes at Different Concentrations

Data for Figure 31 - Concentration Scan

Po110	Flux (1/sq.m.hour)		Robs (%)	
Con\Tube	23	28	23	28
0.85	539.15	447.10	48.08	48.08
2.13	512.85	433.95	33.33	31.25
4.25	486.55	433.95	22.22	21.11
6.37	486.55	420.80	17.54	17.54
8.50	473.40	394.50	13.33	12

EXPERIMENTAL CONDITIONS - ConScan - Po110

Date	88-07-19	Pressure (MPa)	3
Tubes	23/28	Temperature (°C)	30
Salt	NaNO3	Cfv (m/s)	4.5
Salt Conc (g/1)	0.8 - 13	pH	7
Direction of Scan	0.8 --> 13		