THE DEVELOPMENT OF FIXED AND DYNAMIC MEMBRANE SYSTEMS FOR THE TREATMENT OF BRACKISH WATER AND EFFLUENTS

Report to the

Water Research Commission

by

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EXECUTIVE SUMMARY

BACKGROUND AND MOTIVATION

It is well-known that the RSA has limited supplies of water. Membrane technology can be used to both increase the quantity and improve the quality of water available for use. This has already been demonstrated by the successful commercialization of locally developed tubular cellulose acetate RO and polysulphone and polyether sulphone UF membrane systems.

However, newer and more advanced membrane filtration techniques are required, to be able to ensure that the local membrane industry has a wide range of membrane-based products and processes from which to choose; so providing the most suitable and cost-effective solutions to specific requirements.

The basic goal of this research programme was to develope a basis for the provision of membranes and membrane systems for commercialization and application within South Africa.

There are a number of reasons why this membrane development project was embarked upon:

(i) South Africa is a water-poor country and has a high need for the recycling of industrial effluent;

(ii) The need for membrane separation systems in South Africa exceeds the technology transferred to the local commercial company, Bakke Industries, to date;

(iii) Internationally, the development of better and newer membrane systems continues. (One agency in Japan alone devotes $50 million for development of new membrane systems.) If South Africa is to remain competitive in this field of technology, new and improved membranes need to be developed;

(iv) An incentive to develop a local South African membrane-separation industry and the development of a base of local South African expertise would mean the provision of a better service to the South African and African membrane fraternity, operating from a local base;

(v) Owing to the early successes achieved with novel materials for dynamic membranes and because of the low costs of tubular modules which have been realized, the need to create dynamic membrane modules and plants for the local and export market could be of a technological advantage;

(vi) Because newer technologies, e.g. microfiltration, are being developed elsewhere in the world, it is desirable that we should have the opportunity to become involved in the early stages in the development of such membranes.

The benefits expected from the research are to establish (i) a strong and broad-based South African water-treatment company specializing in membrane processes, (ii) wider usage of membrane processes as cost-effective alternatives for ensuring re-use of industrial waste water, (iii) a maintenance base of expertise which will offer solutions to the water re-use problems which may arise in specific industries and (iv) people trained in the field of water treatment by membrane processes. The initial impact of the Membratek Division of Bakke Industries, in the water treatment field, is proof of the soundness of the above outlook.

OBJECTIVES

The following were the objectives of the contract period 1988-1990.

AIM 1: TECHNOLOGY TRANSFER

Playing an active or a supportive role to Membratek.

1. Improvement of existing CA membrane technology

(i) Work on the regeneration of substandard membranes;
(ii) Substitute alternate materials for CA;
(iii) Modify the chemistry of CA for improvement of hydrolytic and bacterial stability;
(iv) Consider alternate methods of preserving membranes;
(v) Analyze membrane and module failure.

2. Improvement of PES UF membrane technology

(i) Determine the role of support fabric in membrane morphology and integrity;
(ii) Investigate systems/environment for range of products;
(iii) Study charged UF membranes;
(iv) Consider module design;
(v) Determine cleaning regimes.

3. TFC RO PVAM membranes

(i) Finalize membrane-production equipment-design in conjunction with Membratek for 3m membranes;
(ii) Supply large batches of chemicals;
(iii) Establish cleaning techniques for membranes;
(iv) Consider regeneration of membranes;
(v) Analyze failure of membranes.

AIM 2: NON-NITROGEN-CONTAINING TFC RO MEMBRANES

(i) Engineer novel membrane materials;
(ii) Design methods for polymer deposition in flat-sheet form;

(iii) Study cross-linking techniques and materials;
(iv) Evaluate integrity: pH, temperature, chlorine;
(v) Consider mathematical optimization of tubular membrane production variables.

AIM 3: DYNAMIC MEMBRANE POLYMER DEVELOPMENT

(i) Create families of novel co- and terpolymers;
(ii) Design novel membranes with specific properties;
(iii) Prepare and test membranes;
(iv) Correlate membrane performance with polymer functionality;
(v) Study membrane performance and consistency of membrane performance in simulation studies with real effluents;
(vi) Create membranes for real cases.

AIM 4: DEVELOPMENT OF A LOW-COST HIGH-PRESSURE DYNAMIC MEMBRANE MODULE

(i) Engineer a nonwoven-fabric-supported microporous PES substrate membrane;
(ii) Develop a parallel-flow membrane pressure support system (ring support concept) and module. Specifications: 6 MPa, 90°C and low permeate side pressure drop;
(iii) Initiate study with thermoset support rings;
(iv) Evaluate prototype ring and module designs at the pressure and temperatures specified and at high concentration levels of oxidative chemicals, alkalis, acids and surfactants;
(v) Finalize ring design;
(vi) Study epoxy systems as alternate support-ring materials and as a potting material;
(vii) Evaluate module housing material and relative cost: GRP, epoxy-coated ferrous and non-ferrous shrouds;
(viii) Evaluate dynamic membrane module and support-membrane system in simulated studies with real effluents.

AIM 5: ESTABLISH PRODUCTION TECHNIQUES FOR THERMAL PHASE INVERSION MEMBRANES

(i) Develop thermal-phase-inversion casting solutions for PES and PP membranes;
(ii) Correlate casting temperatures, rates of cooling and solution composition with membrane morphology and mechanical integrity;
(iii) Adopt and develop the technology for the preparation of new generation membranes for use as:

    (a) TFC membrane supports;
    (b) UF membranes per *se*;
    (c) Micro-porous membranes as support for dynamic membranes;
    (d) Flat-sheet membranes and
    (e) Micro-porous tubulettes (PP).

AIM 6: DEVELOP THE FABRICATION TECHNOLOGY FOR 0,5 TO 2 MM DIAMETER MICROPORE (0,02-0,1 μm) PP AND PES TUBULETTES

(i) Develop extrusion and take-up devices for wet/dry spinning and thermal-phase-inversion fabrication techniques;
(ii) Develop procedures to produce PES tubulettes via the wet-phase-inversion process using wet and/or dry spinning techniques;
(iii) Develop procedures to produce PES and PP tubulettes via the thermal-phase-inversion process;
(iv) Develop techniques to epoxy end-cast the membranes into low-cost plastic modules;
(v) Design automatic cleaning devices for modules;
(vi) Design test equipment to evaluate and modify these membranes into low-pressure dynamic membranes;
(vii) Study membrane performance in simulation studies on real effluents containing:

    (a) suspended solids (MF membranes);
    (b) dissolved solids and organics (Dynamic membranes).

AIM 7: MAINTAIN A WATCHING BRIEF

On matters related to the following:

(1) Amphoteric membranes;
(2) Bi-polar membranes;
(3) Nuclear waste membranes;
(4) Active transport membrane systems.

3. RESULTS AND CONCLUSIONS

The number and diversity of the aims proposed for the project period were, in retrospect, rather ambitious. Most aims have, however, met with a good measure of success; some have been successfully concluded while several warrant further investigation after initial good results. Certain aims received less attention owing to unpredicted situations which arose during the course of the research and which required prompt attention, e.g. removal of foulants from CA membrane surfaces and the dry storage of PES UF membranes. A reallocation of priorities became necessary.

3.1 TECHNOLOGY TRANSFER

3.1.1 IMPROVEMENT IN EXISTING CA MEMBRANE TECHNOLOGY

3.1.1.1 Regeneration of Substandard Membranes

Deteriorated asymmetric N-containing membranes, exhibiting·substandard performance, were treated with either tannic acid or a Bevaloid proprietary product. In both cases membrane rejection was improved by about 10% without forfeiting too much in flux.

Cellulose acetate membranes were treated with a supplemental polymer of poly(vinyl acetate-co-crotonic acid) and crosslinked with $CuCl_2$. In a typical case, RO performance was increased from 52,1% rejection and 88,3 lmd flux to initially 84,0% rejection and 63,2 lmd flux.

3.1.1.2 Substitution of alternate materials for CA

Owing to its greater hydrolytic stability than cellulose diacetate, the use of cellulose triacetate (CTA) for the making of RO membranes was studied.

Strong CTA membranes were made and these exhibited high rejections although fluxes were rather low. Practical problems were encountered with the low solubility of CTA in conventional solvents. The viscosities of the solutions were also very high, further complicating the membrane fabrication process.

RO performance of CTA membranes recorded to date were in the range: 87 - 96% rejection and 226 - 442 lmd flux (tested at 3 MPa).

3.1.1.3 Modification of the chemistry of CA membranes for improvement in hydrolytic and bacterial stability.

Practical problems were encountered during the making of CTA membranes (see 3.1.1.2). Subsequently, in attempts to incorporate the advantages of both cellulose di- and tri-acetate into one membrane type, membranes were made from blends of the two materials, using various fabrication and annealing conditions in efforts to create favourable fabrication conditions.

RO performances ranged from 87,0% rejection and 500 lmd flux to 97,5% rejection and 117 lmd flux.

3.1.1.4 Alternate methods for preserving membranes

Such an investigation was not required, to date, since it had been found by both Membratek and within the IPS CA programme that CA membranes were adequately stored in formaldehyde (0,5%) and in a wet state, which is ensured by the addition of glycerol in quantities of up to 40%.

3.1.1.5 CA Membrane and module failure analysis

Samples of CA membranes from failed Membratek modules were analyzed to determine the cause of membrane failure. The following techniques were used in the autopsies performed on the membranes that had been used in seeded slurry experiments: optical microscopy (differential interference contrast), staining, Fourier Transform Infrared spectroscopy and EDAX analyses of membrane surfaces.

Various findings were made: sections of surface were eroded, surface deposits (mainly aluminium-silicates) were observed and, in cases, hydrolysis was suspected to have taken place.

3.1.1.6 Removal of foulants from membrane surface

Although it was not a topic included in the initial programme, it became necessary to establish effective and safe cleaning techniques for tubular cellulose acetate membranes. This was at the request of Membratek.

The effect which fouling has on the performance of RO membranes can, to a large extent, be counteracted by adopting regular cleaning procedures.

Detergents are commonly used to remove soft organic scaling layers from RO membranes. Care must be taken to then ensure that membrane hydrolysis is not accelerated by the high pH levels of such detergents. A study was therefore conducted to establish safe operating pH levels for organic foulant removal.

Results indicated that rinse solutions of pH 10,4 had a detrimental effect on membrane performance and should not be used. A decline in membrane performance in the cases of other less alkaline solutions tested was also evident, but performance appeared to be subsequently restored after a period of operation under standard conditions, even in the case of a Biotex wash, pH 9,2.

Membranes of tubular configuration have the advantage that they can be cleaned by mechanical means, in conjunction with only moderately alkaline detergent washes.

3.1.2 IMPROVEMENT OF PES UF MEMBRANE TECHNOLOGY

3.1.2.1 Modification of casting systems and casting environment to create range of membranes

Following a meeting of the applications sub-committee for the current project (July 1989) strong emphasis was to be placed on the development of a low molecular mass cut-off UF membrane by the IPS and subsequent transfer of technology to Membratek, who already had a membrane production plant and module production facilities to implement this technology.

Development and manufacture of low cut-off UF PES membranes by IPS was subsequently successfully completed and technical transfer accepted by Membratek. The relevant document "Development and transfer of technology for the manufacture of low cut-off UF membranes" by E.P. Jacobs and H.

Ströhwald (May 1991) describes the techniques for manufacture of the membranes developed by IPS and the successful implementation of such membranes in industry.

3.1.2.2 Determination of cleaning regimes

This work is ongoing as membrane cleaning techniques need to be optimized for each application. The IPS therefore plays an ongoing supportive role to Membratek.

3.1.2.3 Post-treatment of PES UF Membranes

Although the post-treatment of membranes was not one of the original aims of the current project, circumstances led to the search for effective post-treatment procedures. During transportation of wet-stored membranes, problems may arise when storage fluid leaks from the module.

Once the PES membranes dried out, they densified, leading to a decrease in membrane performance. A programme was therefore initiated for the suitable post-treatment of PES UF membranes to prevent deterioration of the membranes as a result of densification when stored in the open.

It was found that dramatic loss in the low-pressure performance of dry-stored PES UF membranes could be prevented or delayed if the membranes were treated in aqueous solutions of either ethylene glycol or glycerol and that post-treatment may also be used to alter the performance of membranes.

3.1.3 TFC RO PVAM MEMBRANES

In the area of composite membrane research and development, three forms of PVAM membranes were fabricated and the following achievements made:

- PVAM/SCl membranes were first made in flat-sheet form and subsequently successfully made in tubular form by a semi-automated process (and found to have better RO performances than the flat-sheet membranes);
- The design of production equipment for making 3 m PVAM/SCl composite membranes was finalized;
- Reaction conditions for the fabrication of two forms of PVAM/SCl tubular membranes were optimized for high retention and flux by means of the mathematical simplex approach;
- A large supply of membrane chemicals was made and stored until required;
- A quality control method for different batches of PVAM was developed, using high resolution ^{13}C NMR spectroscopy.

Typical performances of the three types of membranes were as follows:

TABLE 1:
RO performances of tubular membranes made with precursors PVAM I, PVAM II or PVAM III and crosslinked with SCI

Fabrication formulation	Polymeric precursor	RO performance Salt retention [%]	Flux [lmd]
Optimum for PVAM I/SCI membranes	PVAM I	97,4 ± 0,5	296 ± 5
	PVAM II	62,6 ± 15,0	24 ± 5
	PVAM III	80,3 ± 6,1	25 ± 5,5
Optimum for PVAM II/SCI membranes	PVAM I	94,5 ± 0,3	417 ± 41
	PVAM II	97,4 ± 1,6	491 ± 33
	PVAM III	97,0 ± 1,1	643 ± 74

(Note: Fabrication conditions of the PVAM III/SCI membrane was not optimum).

The salt-retention of PVAM/SCI tubular membranes decreased after 200 h of exposure to feed solutions containing about 5 ppm free chlorine at pH levels of 5,6 and 8,0. The extent of deterioration was less severe for a feed containing up to 6 ppm free chlorine at pH 6,6. These membranes were regarded to be more chlorine tolerant than the early overseas membranes made from PEI, but not as stable as the Film Tec (aramid FT-30) membranes.

Acid conditions also had a detrimental effect on the salt rejection performance of the PVAM/SCI membranes. The optimum pH range for operating these membranes was about 5,5 - 7,5.

3.2 NON-NITROGEN CONTAINING UTF RO MEMBRANES

Research was initiated into the use of PVOH as a membrane-making material, for both reverse osmosis and nanofiltration applications. The aims of the work were twofold: (i) to provide a material(s) with which to replace CA in membranes for certain applications where the hydrolytic stability of CA was insufficient; and (ii) to make composite membranes which were more tolerant to chlorine.

3.2.1 INCORPORATION OF PVOH INTO PVAM MEMBRANES

Adequate low-pressure membranes were made by using an ad-mixture of PVAM + PVOH as precursor. The amount of PVOH in the precursor had a direct influence on the membrane's RO performance. Membranes made from precursor solution of an ad-mixture of PVAM II + 20% PVOH exhibited a typical performance of 97% rejection and 1100 lmd flux at 2 MPa, suggesting their usefulness at possibly even lower pressures.

Membranes prepared from a precursor solution of an ad-mixture of PVAM III + 20% PVOH exhibited a performance of > 90% rejection and 200 lmd flux, when tested at a low operating pressure of 500 kPa with a 2 000 mg/ℓ NaCl feed solution.

3.2.2 MEMBRANES MADE FROM HYDROXYL-CONTAINING POLYMERS AND COPOLYMERS

In recent years there has been a world-wide interest in the fabrication of PVOH membranes; PVOH is an attractive material for the production of RO membranes due to its chemical stability, high hydrophylicity and its film-forming ability. PVOH must, however, be insolubilized by cross-linking or other modification reactions.

In one approach, PVOH was insolubilized by heat treatment in the presence of sulphuric acid. The effect of several fabrication variables on the RO performances of membranes were studied. Early flat-sheet membranes made from PVOH (2%) and H_2SO_4 (0,5%) and heat treated at 125°C, gave average RO performances of 74 - 82% rejection and 820 - 761 lmd flux at 2 MPa with a 2 000 ppm NaCl solution. RO performance ranged from 83 - 91% rejection and 1375 - 620 lmd flux with a 2 000 ppm $MgSO_4$ solution.

Membranes were later made from PVOH crosslinked with potassium persulphate and heat treated. Typical RO performance ranged from 68,4 - 71,0 % rejection and 590 - 717 lmd flux when tested with a 1000 mg/ℓ $MgSO_4$ solution at 2 MPa. Towards the end of this contract period it was found that maturation time of the PVOH/$K_2S_4O_8$ solutions played a significant role in membrane performance. Longer maturation time led to membranes with higher rejections. Useful nanofiltration membranes were made.

3.3 DEVELOPMENT OF POLYMERS FOR THE FORMATION OF DYNAMIC MEMBRANES AND EVALUATION THEREOF FOR THE TREATMENT OF INDUSTRIAL EFFLUENT

Dynamically-formed membranes are RO membranes which are formed in situ by solution chemistry. The membranes comprise a hydrous metal oxide base layer, normally hydrous zirconium (IV) oxide and an organic polyelectrolyte salt rejecting layer, normally poly (acrylic acid) (PAA). Research was initially based on the assumption that the salt rejection by these dynamically formed membrane was solely due to the presence of charge on the membrane. Several substituted acrylic acid homo-co- and terpolymers were synthesized and membranes were made and evaluated.

None of the more highly charged polyelectrolytes showed any improvement over PAA (1 carboxylic acid group per monomer unit) in terms of rejection capabilities, although much higher fluxes were obtained, except in the case of the poly(acrylic acid-co-vinyl acetate membrane). This indicated that a possible way to increase the rejection capabilities of the dynamic membrane was not to increase the charge density but rather to increase the hydrophobic or neutral content of the membrane.

A series of maleic anhydride copolymers were synthesized and used to make dynamic membranes. The more highly charged copolymers exhibited salt rejections far below that of control PAA membranes. Evidence again was that increasing the hydrophobic (uncharged) content section of the copolymer could enhance rejection.

A range of poly (acrylic acid-co-vinyl acetate) (AVAC) polymers and their hydrolyzed form of poly(acrylic acid-co-vinyl alcohol) (AVOH) were synthesized and used in the making of dynamic membranes. The best rejection obtained with AVAC membranes was 97% (AVAC 16) and the best rejection obtained with AVOH membranes was 97% (AVOH 13) (fabrication conditions were not yet optimized). The AVOH copolymer membranes were more stable than the AVAC copolymer membranes; alcohols afforded a possibility for chelation with the hydron zirconium oxide, while the acetate groups did not.

The following developments were considered to have some importance in the field of dynamically formed membranes.

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 1 500 - 2 000 lmd which related to the test facilities used in the course of these studies to a flux of about 1,70 - 2,20 ml/min. Many of the membranes made at IPS were superior in their rejection and flux capabilities to that of the commercially used Acrysol A3 polymer. A set of comparative results is given below (averages of three membranes).

TABLE 2:

Comparison of the performances of the dynamically formed hydrous zirconium IV oxide - Acrysol A3 membranes and an IPS hydrous zirconium oxide - AVOH 86/2 membrane

Time (h)	Rejection (%)		Flux (lmd)	
	Acrysol A3	AVOH 86/2	Acrysol A3	AVOH 86/2
1	89,2	99,0	2016	2424
24	89,0	99,2	1944	2448
48	89,7	99,6	1920	2544
115	-	99,0	-	2712

The membranes appeared to be quite stable and could have a definite practical applicability. This 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 (Tvl., S.A.). The stripped gas liquor varies in make-up from day to day.

After 336 hours of operation there were no signs of membrane degradation. Good rejections of a widely differing spectrum of feed stream constituents were recorded (especially thiocyanates, acids and hydantions) at various water recovery levels. Based on these results it was felt that the AVOH 86/2 dynamic membrane might have an application in the field of industrial effluent treatment.

Hydrous zirconium oxide membranes on a tubular UF support. Satisfactory hydrous zirconium oxide membranes could be formed on tubular UF PES supports. These membranes were formed under the following conditions: flow rate: 2,1 m/s; back pressure: 2 MPa (substantially lower than the standard 6 m/s flux rate and 6 MPa back pressure). Consequently, the formation of low-pressure dynamically formed dual layer membranes were investigated.

Application of dynamic membrane chemistry to other membrane uses. The use of AVAC copolymers as low rejection, low-pressure membranes was demonstrated.

3.4 DEVELOPMENT OF A LOW-COST HIGH PRESSURE DYNAMIC MEMBRANE MODULE

3.4.1 SUBSTRATE MATERIALS DEVELOPMENT

Dynamic UTF membranes have been formed, with reasonable success, inside 12,5mm microporous PES substrate membranes. Some of the results are summarized below:

1) 30% $NaNO_3$ rejection at pH 7 has been obtained repeatedly with membranes formed at linear formation velocities of 1,5m/s and 2MPa feed pressure in 6 x 1m test sections with inorganic zirconium base-membranes.

2) Steady-state pure-water flux performance (200kPa, 0,5 m/s) of the substrate-membrane is reached after 3-4 inorganic base-membrane formation and stripping cycles.

3) Dynamic UTF membranes with 60 to 70% $NaNO_3$ rejection performance (2MPa, 1,5m/s, pH 7) have been formed in 6 x 1m test sections on 30% $NaNO_3$ rejection zirconium base-membranes. (These results compare well with those of control membranes formed inside 2 x 1,5m tubular porous stainless steel (Carre) substrates).

4) The $NaNO_3$ retention (pH 3,5) of the first single-layered Zr-membranes ranged between 22% up to 42%, on occasion, for the different substrates tested. Average retention values of 39% was easily obtained on "re-membraning" the various substrates evaluated.

5) The salt retention of dual-layer membranes did not differ much for substrates with 80% MMCOs between 6 000 and 40 000 dalton (evaluated against PEG and PVP). The highest point-reading for dual-layer membrane retention was 82%, and that was achieved on both extremes of the above range.

6) Some correlation was found between the 3MPa permeate flux of the first Zr-layer deposited and the UF characteristics of the substrate. All permeate fluxes, however, showed a steady decline after each "re-membraning" step. After four Zr-membrane replacements, the initial correlation observed had disappeared.

7) The dynamic membrane layers were *dynamic* in the sense that some loss (10% and greater) of membrane properties were observed over periods of between 18h and 67h of

operation on fresh $NaNO_3$ solutions. (All evaluations were performed in close-loop tests systems).

The experimental results show that synthetic UF membranes can be used as substrates for dynamic membranes. The possibility of achieving still higher salt retention with lower cut-off Kollidon 30 UF membranes needs to be investigated.

The consistency in performance of the dynamic membranes formed was good, although a constant reduction in PWF was noticed after each membrane stripping cycle. However, it appeared as if asymptotic values are reached after a number of formation and stripping cycles.

A problem in the use of these membranes stemmed from the use of polyester as a support material for the UF membrane since hydrolysis of the polyester at the high pH-levels prevailing during membrane stripping cycles can cause weld-seam failure. However, no problem was experienced, to date, at the low pH conditions that prevailed during Zr formation and stripping.

3.4.2 TUBULAR MEMBRANE SYSTEMS DEVELOPMENT

A higher cross-flow velocity can be achieved in tubular membrane modules with the present design of the test cell and pump capacity by fitting a torpedo device inside the membrane element; the membrane cross-section flow geometry is thus altered from circular to annular. The higher shear rates caused by the increase in velocity leads to the formation of dynamic membranes with improved performance.

The feasibility of casting externally coated tubular membranes was demonstrated but efforts to incorporate these membranes into a module design have been unsuccessful to date.

Tubular poly(acrylic acid) dynamic membranes, formed on 500mm PES substrate membrane test sections, showed 85% and higher percent salt-rejection. In some tests over 90% salt rejection has been obtained with the use of turbulence promoters (3MPa, 2 000 $NaNO_3$).

The work was subsequently concluded because of the inability of the PET substrate material to withstand the harsh alkaline cleaning and stripping regimes of the polyelectrolyte and Zr (IV) membrane layers.

Although the work on the dynamic membrane module development was curtailed, much of the know-how developed could be applied in other areas of the programme. Some of the techniques used in the end-potting of tubular membranes, for example, was initially applied in the fabrication of capillary membrane modules.

3.5 FABRICATION TECHNOLOGY FOR CAPILLARY MEMBRANES

Capillary membranes can be produced. However, the problems that still exist concern both membrane and module production; special emphasis is on potting compounds, potting procedures and in fibre mechanical strength and consistency in performance. Initial tests with the capillary membranes have proved the following advantages of the system:

i) The membranes may be cleaned with high concentrations of NaOH because of the absence of a PET support fabric, and

ii) they may be made to very low MMCO specifications, because the low fluxes can be counteracted by higher surface areas.

The above aspects make it clear that capillary membranes need a high priority in any contract for the development of new membrane-fabrication technology.

3.6 MAINTAINING A WATCHING BRIEF

Pervaporation

Sasol was interested in pervaporation as an alternate means of removing alcohols from hydrocarbons. To date, water was used to wash out the alcohols. Novel co-polymeric membranes were created, a pervaporation test apparatus designed and constructed and both IPS membranes and commercially available membranes tested for their separation ability of ethanol from hexane.

It was found that membrane performance depended largely on the chemical nature of the membrane material. The IPS terpolymer poly(vinyl acetate-co-hydroxyethyl acrylate-co-acrylic acid) appeared to be a useful membrane material.

RECOMMENDATIONS FOR FUTURE RESEARCH

Following on from progress made and results achieved during the 1988 - 1990 project period, recommendations for future research should include the following:

1. Pursue investigations into the regeneration of substandard membranes, using various supplementary layers and/or membrane treatments;

2. Chemically modify the cellulose diacetate material currently used in membrane fabrication, by carrying various chemical reactions on CA, and use this modified material to make more robust CA RO membranes. Evaluate its suitability and the RO performance of such membranes;

3. Continue to research and develop PVOH-based membranes. Test their robustness, in terms of chlorine and pH tolerance;

4. Optimization of membrane-formation conditions of several of the dynamic AVAC and AVOH copolymer membranes, and possibly investigate the use of mixed hydrous metal oxides for the basic dynamic membrane.

At present only tubular CA RO membranes and a series of tubular PES UF membranes are locally available, as result of research carried out at IPS. It will therefore be necessary to develop newer membrane systems which could fulfil the requirements of the market. It is proposed that research be conducted into the creation of a new family of low-pressure membranes, capable of operating at pressures below 2 000 kPa. Two classes of membranes should be considered:

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

(b) a low to medium NaCl - rejection nanofiltration (NF) membrane, exhibiting 40 - 60% rejection at operating pressures of 500 - 1000 kPa.

The following types of synthetic membranes were to be used as starting points from which to aim for the above requirements:

PVOH - based membranes and PVAM - based membranes which were to be modified by the addition of hydrophilic precursors.

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LIST OF ABBREVIATIONS

AHEA	Poly(acrylic acid co-hydroxymethyl acrylate), 10% acrylic acid in copolymers
AVAC	Acrylic acid-co-vinyl acetate copolymers
AVOH	Poly(acrylic acid-co-vinyl alcohol) copolymers
CA	Cellulose acetate
DAB	1,3-Diaminobenzene
EDA	1,3-Diaminobenzene
DETA	Diethylenetriamine
FTIR	Fourier Transform Infrared
IPC	Isophthaloyl dichloride
$K_2S_2O_8$	Potassium persulphate
MMCO	Molecular mass cut-off
MVE-alt-MAH	Methyl vinyl ether-alt-maleic anhydride copolymers
NaOCl	Sodium hypochlorite ("Jik")
NF	Nanofiltration
PEI	Polyethyleneimine
PES	Poly(arylether sulphone)
PIP	Piperazine
PP	Polypropylene
PS	Poly(bisphenol-A-sulphone)
PSSNa	Polystyrenesulphonate-Na salt
PVAC	Polyvinylacetate
PVACVAPE	Polyvinylacetate-vinyl-aminophenylether
PVAM	Poly-2-vinylimidazoline
PVOH	Polyvinylalcohol
PVP	Polyvinylpyrollidone
RO	Reverse Osmosis

SCl	3,5 Dichlorosulphonylbenzoyl chloride
SGL	Stripped gas liquor
TEA	Triethylamine
TMC	Trimesoylchloride
UF	Ultrafiltration
UTF	Ultra-thin-film

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1. INTRODUCTION

1.1 BACKGROUND

The RSA has limited supplies of one strategic commodity that affects the lives of all South Africans, namely, water. We, as scientists are compelled to make the RSA self-sufficient with regard to technologies that can be used to augment the volume of water available for use. In the field of membrane systems, membrane scientists can play a key role in making the country self-sufficient in the areas of waste water management, water treatment and by-product recovery. This has already been demonstrated by the successful commercialization of the locally developed tubular cellulose acetate (CA) membrane system and by the advances made with ultrafiltration (UF) systems.

Although South Africa has already made great progress in effluent treatment, newer and more advanced techniques are required, and therefore further aspects of membrane separation processes should be considered. Membrane scientists need to ensure that the local membrane industry will have a full range of processes and products from which to choose, to meet specific customer requirements, as well as the expertise with which to handle South Africa's water-associated problems which exist at present and which will escalate in the future. We should be able to offer more than one solution to any effluent problem in order that an optimum and economical solution can be found. It is imperative not merely to make paper findings but also to prove the viability of findings in the field. It is important, therefore, for industry to be able to get a partial "package" from the research effort before they go into production. It is suggested that this "package" should include the know-how of how to fabricate selected membranes, limited on-site effluent evaluation, with consideration for such aspects such as ageing, fouling and cleaning of the membrane and how the membrane should be handled.

Since there is now a local commercial company which can handle basic membrane fabrication processes, e.g. the production of tubular CA membranes, the time is now ripe for progress to be made in other directions. It is important to make membranes which can be used in the treatment of specific effluents, e.g. phenolic waste streams from Sasol, fish-stick waste water, dairy whey, and winery effluent. South African membrane technology is already well accepted and advanced in the treatment of municipal effluent. We realize that while it is impossible to compete with the likes of the $50 million municipal effluent research effort in Japan, it is important that systems already proved in South Africa should be advanced still further.

The viability of products and technology developed in contracts entered into with the WRC in the past have already been proved. This has been evident in the industrialization of membrane processes, which has provided solutions to many industrial problems. As yet, however, we have only scratched the surface, and a great amount of work remains to be done to enable us to improve the state of the art in South Africa, in order that we will be able to alleviate our own water problems and make us less dependent on overseas products and expertise.

In investigations aimed at greater SA independence in the field of water management with membrane systems, a number of areas of research have been cited. Those, which the IPS proposes to consider are outlined below, in order or priority.

1.2 OBJECTIVES

The following were therefore proposed aims and related tasks for the current contract period.

1.2.1 AIM I: TECHNOLOGY TRANSFER

Playing an active or a supportive role to Membratek, attention was to be given to the following three areas with the aim of working towards technical transfer from IPS to Membratek.

1.2.1.1 Improvement of existing CA membrane technology

(i) Work on the regeneration of substandard membranes;
(ii) Substitute alternate materials for CA;
(iii) Modify the chemistry of CA for improvement of hydrolytic and bacterial stability;
(iv) Consider alternative methods of preserving membranes;
(v) Analyze membrane and module failure.

1.2.1.2 Improvement of PES UF membrane technology

(i) Determine the role of support fabric in membrane morphology and integrity;
(ii) Investigate systems/environment for range of products;
(iii) Study charged UF membranes;
(iv) Consider module design;
(v) Determine cleaning regimes.

1.2.1.3 TFC RO PVAM membranes

(i) Finalize membrane production equipment design in conjunction with Membratek for 3M membranes;
(ii) Supply input to chemical production;
(iii) Establish cleaning techniques for membranes;
(iv) Consider regeneration of membranes;
(v) Analyze failure of membranes.

1.2.2 AIM 2: NON-NITROGEN-CONTAINING TFC RO MEMBRANES

(i) Engineer novel membrane materials;
(ii) Design methods for polymer deposition in flat-sheet form;
(iii) Study cross-linking techniques and materials;
(iv) Evaluate integrity: pH, temperature, chlorine;
(v) Consider mathematical optimization of tubular membrane production variables.

1.2.3 AIM 3: DYNAMIC MEMBRANE POLYMER DEVELOPMENT

(i) Create families of novel co- and terpolymers;
(ii) Design novel membranes with specific properties;
(iii) Prepare and test membranes;
(iv) Correlate membrane performance with polymer functionality;
(v) Study membrane performance and consistency of membrane performance in simulation studies with real effluents;
(vi) Create membranes for real cases.

1.2.4 AIM 4: DEVELOPMENT OF A LOW-COST HIGH-PRESSURE DYNAMIC MEMBRANE MODULE

(i) Engineer a nonwoven-fabric-supported microporous PES substrate membrane.
(ii) Develop a parallel-flow membrane pressure support system (ring support concept) and module. Specifications: 6 MPa, 90°C and low permeate side pressure drop.
(iii) Initiate study with thermoset support rings;
(iv) Evaluate prototype ring and module designs at the pressure and temperatures specified and at high concentration levels of oxidative chemicals, alkalies, acids and surfactants;
(v) Finalize ring design;
(vi) Study epoxy systems as an alternative support-ring materials and as a potting material;
(vii) Evaluate module housing material and relative cost: GRP, epoxy-coated ferrous and non-ferrous shrouds;
(viii) Evaluate dynamic membrane module and support-membrane system in simulated studies with real effluents.

1.2.5 AIM 5: ESTABLISH PRODUCTION TECHNIQUES FOR THERMAL PHASE INVERSION MEMBRANES

(i) Develop thermal-phase-inversion casting solution for PES and PP membranes;
(ii) Correlate casting temperatures, rates of cooling and solution composition with membrane morphology and mechanical integrity;
(iii) Adopt and develop the technology in the preparation of new generation membranes for use as:

(a) TFC membrane supports;
(b) UF membranes per *se*;
(c) Micro-porous membranes as support for dynamic membranes;
(d) Flat-sheet membranes and
(e) Micro-porous tubulettes (PP).

1.2.6 AIM 6: DEVELOP THE FABRICATION TECHNOLOGY FOR 0,5 TO 2 MM DIAMETER MICRO-PORE (0,02-0,01 μm) PP AND PES TUBULETTES

(i) Develop extrusion and take-up devices for wet/dry spinning and thermal-phase-inversion fabrication techniques;
(ii) Develop procedures to produce PES tubulettes via the wet-phase-inversion process using wet and/or dry spinning techniques;
(iii) Develop procedures to produce PES and PP tubulettes via the thermal-phase-inversion process;
(iv) Develop techniques to epoxy end-cast the membranes into low-cost plastic modules;
(v) Design automatic cleaning devices for modules;
(vi) Design test equipment to evaluate and modify these membranes into low-pressure dynamic membranes;
(vii) Study membrane performance in simulation studies on real effluents containing;

(a) suspended solids (MF membranes);
(b) dissolved solids and organics (Dynamic membranes).

1.2.7 AIM 7: MAINTAIN A WATCHING BRIEF

On matters related to the following:

(1) Amphoteric membranes;
(2) Bi-polar membranes;
(3) Nuclear waste membranes;
(4) Active transport membrane systems.

1.3 MOTIVATION

In terms of water re-use, membrane processes offer viable alternatives to many of the biological-type waste treatment processes presently used. The processes are also alternatives to distillation. Often they offer the only cost-effective processes for the treatment of industrial effluents. The range of membrane-process uses is too large to discuss simply. General areas of usage under discussion are: removal of salt from seawater, brackwater or industrial waters; removal of organics and toxic organics, together with salts, from industrial waters; upgrading of secondary sewerage effluent; ultrafiltration of colloids from industrial waters or microfiltration of colloids and suspended solutes from industrial and sewerage waters.

The basic goal of this research programme should be the provision of membranes and membrane systems for commercialization and application within South Africa. The extent to which they can solve South African waste water problems is already evident from the successes being achieved by the Membratek Division of Bakke merely with the one membrane system (CA) to date.

There are a number of reasons why this current project should be embarked upon:

(i) South Africa is a water-poor country and has one of the highest needs for the recycling of industrial effluent;

(ii) The need for membrane systems in South Africa far exceeds the technological level presently realized with technology transferred to Bakke Industries to date;

(iii) Internationally, the development of better and newer membrane systems has not ceased. (One agency in Japan alone devotes $50 million for development of new membrane systems.) If South Africa wishes to remain competitive in this field of technology, new and improved membranes will remain constant requirements;

(iv) It is often difficult to treat South African effluents by means of the technology offered by many of the competing overseas companies. Besides the cost of overseas technology being very high, overseas companies might not always be in the position to service their plants in South Africa, giving rise to operational problems. This serves as a great incentive to develop a local South African membrane-separation industry and the development of a base of local South African expertise;

(v) Because of the successes achieved with the novel materials for dynamic membranes and because of the low costs of modules which have been realized, the need to create dynamic membrane modules and plants for the local and export market could be of technological advantage;

(vi) Because newer technologies, in terms of microfiltration, are being developed elsewhere in the world, it is desirable that we should have the opportunity to become involved in the early stages of such developments. All the areas of the application of microfiltration have, to date, hardly been touched.

The expected benefits of the research should be the establishment of a stronger and a broader-based South African water-treatment company specializing in membrane processes, wider usage of membrane processes as cost-effective alternatives for ensuring re-use of industrial waste waters, and the maintenance of an expertise data base which will provide solutions to the water re-use problems which may arise in specific industries. The potential result is therefore an even bigger South African membrane industry solving more and more specific problems peculiar to South Africa and in so doing, creating more re-use of water and lower overall industrial water demand. The initial impact of the Membratek Division of Bakke in this regard is proof of the soundness of the above assertions.

SECTION 1: TECHNOLOGY TRANSFER

2. IMPROVEMENT OF EXISTING CA MEMBRANE TECHNOLOGY

2.1 REGENERATION OF SUBSTANDARD MEMBRANES

2.1.1 BACKGROUND

The technology upon which this research work was based followed from the results of earlier local studies **[1-3]** by Pienaar and Sanderson of the Institute for Polymer Science.

Supplemental coatings of low molecular mass copolymers of vinylacetate and crotonic acid were applied to CA RO membranes to enhance reduced membrane performance. There was no request by Membratek for technology transfer of the progress made in this field. There was, however, a request from COMRO for the IPS to assist them in carrying out autopsies on their failed membranes, used in their SPARRO process, and to suggest any possible methods of treatment.

2.1.2 RESULTS AND DISCUSSION

In summary, a number of autopsies were carried out on the tubular CA membrane samples that had originated from the COMRO process. Microscopic analyses of the membrane surfaces indicated that erosion had taken place. Hydrolysis of the membranes was also evident but, at the time, there was no indication as to whether the hydrolysis was caused by process conditions (redox potential of the feed water or spillage of the alkaline feed water) or was due to microbial degradation of the membranes. A detailed report was submitted to COMRO stating the findings which the IPS had made **[4]**. In the light of the findings, it was suggested that application of a protective coating to the membrane surface might reduce or prevent erosion of the membrane surface. A membrane regeneration experiment was then carried out by IPS in an attempt to restore the average performance of a set of 6 "deteriorated" membranes, using poly(vinyl acetate-co-crotonic acid) crosslinked with $CuCl_2$.

Original RO performance was:	57,1% retention; 88,3 lmh flux;
Restored RO performance was:	88,9% retention; 63,2 lmh flux;
(Test conditions:	2 MPa, 2000 ppm NaCl, 20°C)
After 67 h testing, RO performance was:	84,0% retention.

Subsequently, attempts were made to improve the performance of asymmetric N-containing membranes (membranes obtained from SEPAREM) by treating them, in situ, with either tannic acid (a product of the reaction of trihydroxy benzoic acid and sugars or a Bevaloid research chemical RD 116/188 + $CuCl_2$.

Experimental details: membranes used, application of coatings and testing of membranes are described elsewhere **[5]**.

2.1.2.1 Tannic acid treatment

The RO results of "degraded" membranes, treated with tannic acid are given in Tables 1 and 2.

<u>TABLE 1</u>:
The effect of tannic acid post-treatment on the RO performance of N-containing membranes (first treatment)

	1	2	3	4	5	6
Initial Rejection R (%) Flux J (lmd)	84.9 766	84,5 729	84,6 833	87,7 760	69,6 924	88,2 613
RO performance after tannic acid treatment for two hours, $CuCl_2$ treatment for 18 hours						
Test time (h) R (%) 5 J (lmd)	91,9 638	92.7 591	91,5 691	93,5 644	79,6 710	94,8 506
R (%) 48 J (lmd)	91,7 636	92,4 584	91,1 686	93,4 644	79,0 708	94,7 504
R (%) 195 J (lmd)	91,4 668	92,1 626	90,8 729	93.0 674	78.5 753	94,6 541

<u>TABLE 2</u>:
The effect of tannic acid post-treatment on the RO performance of N-containing membranes (second treatment)

	1	2	3	4
Initial Rejection R (%) Flux J (lmd)	85,2 659	81,3 847	83,1 1210	85,3 85,3
Tannic acid treatment for 30 minutes, $CuCl_2$ treatment for 30 minutes				
Test time (h) 73 R (%) J (lmd)	95,8 673	94,0 535	90,2 1073	92.2 1038

It is clear from the above that the tannic acid treatment does improve the membrane performance. Comparing the results in Tables 1 and 2, it would appear as though a treatment period of only 30 minutes is enough for the supplemental coating to deposit.

2.1.2.2 Bevaloid RD 116/188 treatment

The RO results of "degraded" membranes, treated with RD 116/188 are given in Table 3.

TABLE 3:

RO performance results of N-containing membranes post-treated with RD 116/188

		1	2	3	4
Initial					
Rejection R (%)		91.9	88.8	87,6	87,0
Flux J (lmd)		1170	900	1330	1260
RO performance after RD 116/188 treatment for 30 minutes, CuCl$_2$ treatment for 30 minutes					
Test Time (h)					
	R (%)	98,1	97,6	97,2	96,9
73	J (lmd)	965	727	1040	990

2.1.3 CONCLUSIONS

Both tannic acid and RD 166/188 proved effective in improving the RO performances of "degraded" SEPAREM N-containing asymmetric membranes.

Although these initial results look good, long-term tests still require to be carried out to determine the stability of these coatings.

2.1.4 TUBULAR MEMBRANE EVALUATION KIT

One of the experimental advantages of a tubular membrane evaluation kit would be that the treatment of membrane with supplemental polymer coatings could be simply investigated and the lifetime and effectiveness of such a treatment could be established.

Such a tubular membrane evaluation kit will therefore be described here (in this section).

2.1.4.1 Introduction

A tubular membrane test-cell facility was devised and made available and which allowed a series of short-length tubular membranes to be evaluated, alongside full-sized modules, during a pilot plant study. The test-cell facility is equipped with three valves to allow the replacement or inspection of test membranes, without affecting the operation of the main plant. The test cell is connected upstream of the pressure regulating valve, where its presence will not interfere with the operation of the plant.

2.1.4.2 The tubular test cell facility

The design of a tubular membrane test-cell attachment is shown in Figure 1. The unit consists of tubular membrane test cells which are connected in a series flow-through arrangement. The test cells are of 316 stainless steel design, and similar to the cells used by the Institute for Polymer Science. Each cell house a 13 mm diameter membrane of 500 mm length. Perforated 316 stainless steel tubes are used as the pressure support, and rubber grommets are used to seal the membrane ends against screw-on flanged connectors. A clear plastic shroud encases each cell, which allows for individual evaluation of single cell performance.

The unit can be isolated from the process stream by means of three ball valves. The unit is also equipped with further valves and ports for external connections to facilitate cleaning or coating studies. A connecting point is provided for a pressure gauge.

2.1.4.3 Experimental advantages

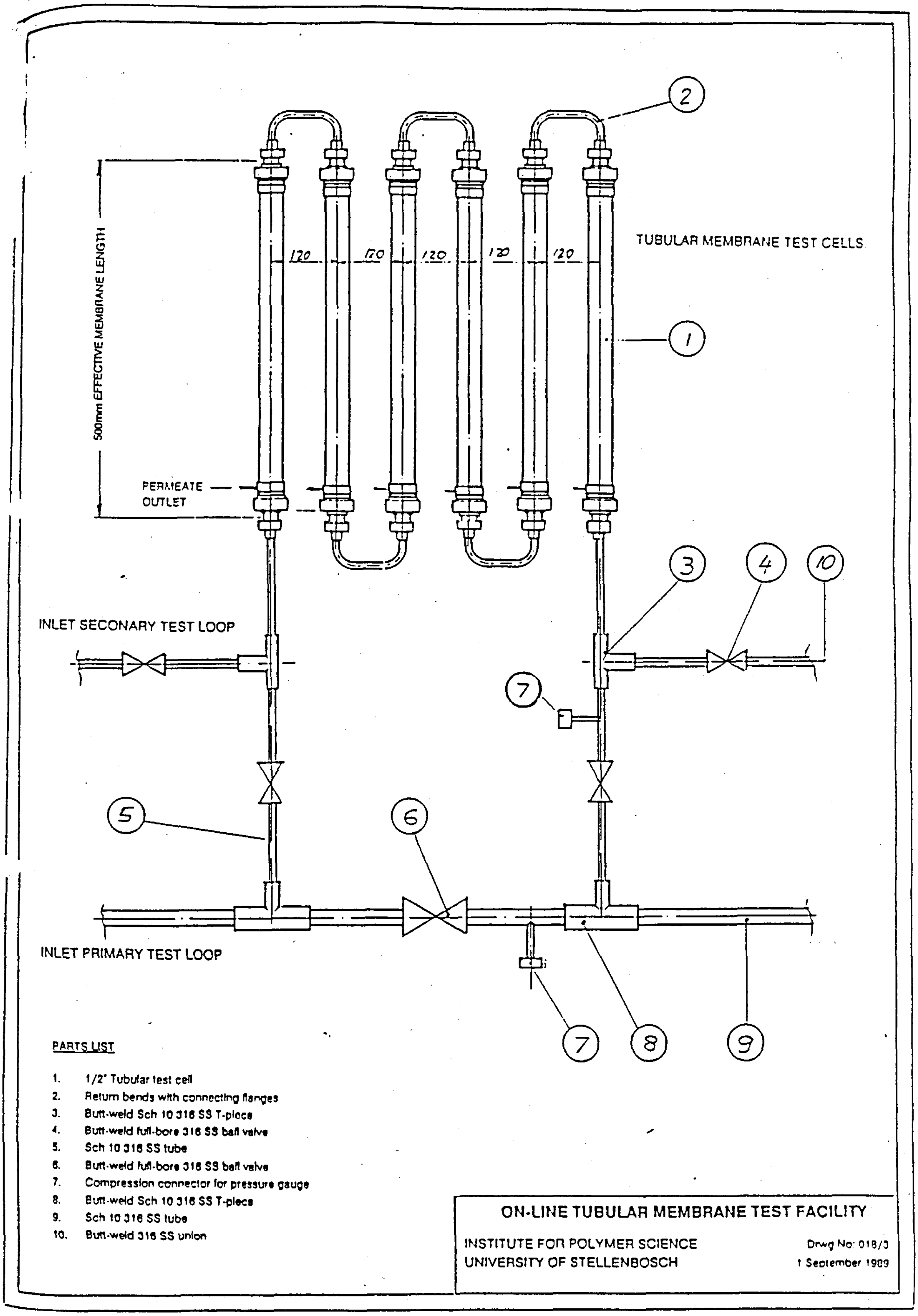
The test facility offers the following advantages to the investigator:

1. During the operation of a pilot plant, the need often arises for membranes to be withdrawn from service to allow their closer inspection. The test cell unit allows short-section membranes to be withdrawn from service, without interrupting the operation of the plant, or incurring the cost of unnecessarily withdrawing a full-sized module from service.

2. The test cell unit operates on the concentrated reject stream. As such, the membranes are operated under the most adverse conditions that exist within the plant. As the membrane-unit can be isolated from the plant, an opportunity makes itself available to conduct a study on effective membrane cleaning regimes.

3. Supplemental polymer treatment to restore/improve the performance of deteriorating membranes before replacement of membrane modules should be considered. The test unit offers the advantage that the treatment of membranes with supplemental polymer coatings can be investigated and that the lifetime and effectiveness of such a treatment can be established.

4. The high concentration of particulate material present in e.g. the SPARRO process water causes erosion of the skin surface-layer of the membranes. Different membranes (gel-coated membranes, membranes from different materials of construction etc.) can be compared in the cell-unit to determine relative degrees of weathering under the same feed conditions.



PARTS LIST

1. 1/2" Tubular test cell
2. Return bends with connecting flanges
3. Butt-weld Sch 10 316 SS T-piece
4. Butt-weld full-bore 316 SS ball valve
5. Sch 10 316 SS tube
6. Butt-weld full-bore 316 SS ball valve
7. Compression connector for pressure gauge
8. Butt-weld Sch 10 316 SS T-piece
9. Sch 10 316 SS tube
10. Butt-weld 316 SS union

ON-LINE TUBULAR MEMBRANE TEST FACILITY

INSTITUTE FOR POLYMER SCIENCE Drwg No: 018/3
UNIVERSITY OF STELLENBOSCH 1 September 1989

FIGURE 1:
On-line tubular membrane test facility

2.2 CA MEMBRANE AND MODULE FAILURE ANALYSIS

2.2.1 BACKGROUND

Although IPS had not been directly asked to launch a study into the failure of the Membratek CA modules, it did carry out analyses of samples of tubular membranes which had failed.

With regard to the study of membrane failure analysis, most of the work was done on the COMRO membranes (already mentioned in section 2.1).

2.2.2 ANALYSIS OF MEMBRANE SAMPLES

2.2.2.1 Introduction

Two sets of membrane samples were received from Membratek for analysis, one set marked Module 3 (881295) and the other Module 4 (881502); each set consisted of membranes taken from the inlet, center and outlet of each module.

2.2.2.2 Optical microscopy - Differential Interference Contrast (DIC)

Sample Preparation

Samples were prepared for optical microscopy by cutting 6 cm-lengths from the various tubes. These samples were mounted on glass slides and, in order to get some indication of possible foulant deposits, the surfaces of the membrane samples were never touched by hand during sample preparation.

The samples were allowed to dry out naturally and were sputter-coated with gold before being analyzed.

Observations

There were marked differences between the appearances of membranes from Modules 3 and 4 and those of Modules 1 and 2 received previously. Radial bands of up to 4 mm, and dull in contrast to the remainder of the membrane films which were still shiny in appearance, extended at intervals across the length of the sample analyzed. Initially this was observed only after sputter-coating with gold. However, when once observed, it was also recognized on other samples once the surfaces of the membranes were wiped clean of any loose surface deposits or debris.

DIC micrographs were taken of sections of the various samples received (1000 x magnification). As in the case of Modules 1 and 2 earlier investigated **[4]**, erosion marks, caused by particle impingements were seen.

Deposits were present in a greater or lesser extent on all of the samples analyzed. (Module 3 seems to be less affected than Module 4). Cases were observed where deposits seem to have nucleated from scourmarks left by larger-sized particle impingement on the membrane surface.

Except for brief examination during EDAX analysis, the membranes were not investigated by means of SEM. During optical microscopy evaluation of the various samples, no obvious evidence was found of gross structural damage to the membrane body.

However, a strange phenomenon was noticed during the analysis of samples from Module 4 membranes. Previously, the marks on the membrane surfaces were all essentially unidirectional, and clearly in the axial direction of fluid flow. In Module 4, the membrane surface carried impression which were clearly not unidirectional. A possible explanation for these randomly orientated marks is that they were formed by crystals of some sort, which had been forced into the membrane surface under the action of hydrostatic pressure. However, no evidence of the presence of long-shaped crystals could be found anywhere during microscopic analysis.

2.2.2.3 Staining

Samples from the various membrane sets were rinsed clean with a 5% acetic acid solution and rinsed thoroughly before being stained with identification stains obtained from Du Pont.

In comparison to membranes from the earlier received modules, membranes from Modules 3 and 4 differed in the way in which they stained under the action of the dye. This was regarded as some indication that the chemistry of the membrane material may have been affected.

2.2.2.4 Fourier Transform Infrared (FTIR)

To gain some proof for the above observation, membrane samples were taken for FTIR analysis. The samples were analyzed using the ATR facility on the instrument as the membrane films abstracted from the support fabric were not clear. Unfortunately the spectra obtained during this part of the exercise were of little value due to low immission levels.

However, during experiments to dissolve membrane films taken from Modules 3 and 4 and membrane films taken from freshly produced CA membranes (Membratek supplied) and virgin CA 398-10 cellulose di-acetate powder (IPS stock); differences in solubility behaviour were noticed.

Virgin CA membrane films and CA powder dissolved in acetone and swelled in chloroform. However, module 3 and 4 samples only swelled in acetone, whereas chloroform left the films unaffected.

This was thought to be in further evidence that the chemistry of the membranes had been modified, although it could not be quantified due to the unavailability of the FTIR equipment.

2.2.2.5 EDAX analysis of deposits on membrane surface

Specimen membranes were carbon-coated for elemental analysis of surface deposits by EDAX.

A representative elemental analysis of the deposits is shown in an EDAX printout were obtained. According to this analysis there is little presence of $CaSO_4$ in the deposit. Deposits appear mainly to consist of aluminium and silicon (probably aluminium silicates), and to a lesser extent iron and calcium (sulphates). (In retrospect, the tiny (< 0,1 μm) crystals that were seen during polarized light microscopy is therefore most probably of quartz origin).

2.2.2.6 Conclusions

Without the benefit of comparing the analysis given to that of a module that has accumulated the same number of operating hours, and which is still exhibiting good performance, the following can be said:

1) The surfaces of the analyzed membranes appeared to be eroded to a greater extent than those of Modules 1 and 2 (refer ref. **[4]**).

2) Surface deposits, consisting mainly of aluminium-silicates, were observed, especially in the case of Module 4.

3) According to solvent solubility differences, the COMRO samples are believed to be chemically different from the virgin membrane samples and powder analyzed. (However, the latter is very much dependant on whether the same source and grade of material was used a reference material).

4) Based on the samples analyzed from Modules 3 and 4, no reason, other than the possibility of hydrolysis, can be offered for the lower performance of the membrane specimens received.

2.2.2.7 Recommedations

1) The Institute should approach Membratek for 500 mm-sections of membranes from Modules 3 and/or 4. The membranes will be coated with supplemental polymers to establish whether it would be possible to restore the performances of the membranes. If positive results are obtained, arrangements can be made for module evaluation and dissemination of the results of the study.

2) The IPS can make tubular membrane test cells (400 - 500 mm long) available to COMRO, on either a hire or purchase basis, to allow close observation of single membrane performance. (Such cells can be piped into the end of a module train). This offers the advantage that single membranes can be removed for inspection at the first sign of performance deterioration. This might allow some insight into possible causes of membrane failure.

2.3 ALTERNATE METHODS FOR PRESERVING MEMBRANES

Such an investigation was not required, to date, since it had been found by both Membratek and within the IPS CA programme that CA membranes were adequately stored in formaldehyde (0,5%) and in a wet state which is ensured by the addition of glycerol in quantities of up to 40%.

2.4 CHEMICAL MODIFICATION OF CA - TO IMPROVE HYDROLYTIC AND BACTERIAL STABILITY

2.4.1 BACKGROUND

During a recent overseas visit to the membrane production subsidiary of Eastman Kodak, namely Fastex, it was found that they were producing two-inch spiral wrap cellulose triacetate (CTA) membranes. These membranes had higher hydrolytic stabiilty than the cellulose diacetate (CA) membranes known and produced to date. A typical RO performance capability of this membrane was 97,7 ± 0,3% rejection and 330 ± 6 lmd flux (2 MPa, 20°C, 2000 ppm NaCl feed solution). The specific grade of CTA and casting solution composition was, of course, classified information.

Although CA membranes have to date, provided adequate membranes at reasonable cost, they posses several shortcomings; low chemical and thermal resistance leading to hydrolysis of the acetate groups, ease with which it biodegrades and a marked decrease in flux with time of operation.

CTA posesses a much higher chemical stability and is not as readily biodegraded. CTA membranes are mechanically strong and capable of high retention performances, although fluxes may be rather low. Use of CTA as membrane forming polymer has however been limited, to date, due to the problems encountered with the solubility of CTA in the conventional solvents. Research into this problem has recently show which solvents/solvent systems may be suitable for the casting of CTA membranes. By adding selected swelling agents to the casting solution, membranes fluxes can also be improved.

A study was therefore begun by first carrying out an extensive literature survey into establishing what technologies existed for the production of CTA membranes. Several formulations were selected and reproduced at IPS to make CTA membranes. Unfortunately the specific grade of Eastman Kodak CTA required was not available in SA to us at the time. (Eastman Kodak had withdrawn this agency from South Africa.) A sample of Dow CTA was obtained and this was used to prepare casting solution from which membranes were made and then tested for their RO performance. Practial problems were encountered with the low solubility of CTA and high viscosity of casting solutions.

A detailed literature survey of the making of CTA RO membranes, including CA/CTA blend membranes, and their performances was carried out **[6]**. A summary of the most important findings is presented in Table 4.

TABLE 4:

CTA Membranes: Casting solutions and RO performances
(ex literature) **[6]**

Membrane number	1	2	3
Reference	Nguyen [7]	Joshi [8]	Joshi [8]
CTA (mass %)	10,0	12,95	12,95
Dichloromethane	70.0	-	-
Magnesium perchlorate	6,0	-	-
Dioxane	-	62,26	62,26
Acetone	-	20,47	20,5
Maleic acid	-	4,32	-
Maleic acid anhydride	-	-	4,3
Methanol	14,0	-	-
Evaporation time (min)	0.5	1,5	1,5
Coagulation bath time	MeOH/H_2O	H_2O	H_2O
Annealing bath	H_2O	H_2O	H_2O
Annealing temperature (°C)	-	90	90
NaCl Retention (%)	85,5	97,8	98-99
Flux (lmd)	160	142,6	126-183
Pressure (KPa)	1724	6900	6900
NaCl concentration (ppm)	3500	30,000	35000

Several blend membranes of CA + CTA were also made and tested. By using blends, it was envisaged to improve the hydrolytic stability of CA membranes and overcome the problems of solubility, encountered in the making of CTA membranes. As the two CA polymers had very different solubility parameters, careful consideration had to be given to the choice of suitable solvent systems.

A detailed report on the research work carried out at IPS into CTA and CA/CTA blend membranes including early test results is available **[9]**. Highlights thereof, alone will be presented here.

2.4.2 EXPERIMENTAL

Several flat-sheet membranes, both CTA and blend CA/CTA, were hand-made from selected casting conditions with varying compositions.

Casting solutions were filtered through a 1 μm stainless steel filter, prior to use.

Membranes were coagulated in a waterbath at 0°C for 1 h and then stored in a waterbath at 4°C prior to testing.

Composition of various casting solutions used are shown in Table 5.

TABLE 5:

Typical compositions of casting solutions used to make CTA and CA/CTA blend membranes

Components of casting solutions [mass %]	F_1	F_2/T_1	F_3
Cellulose triacetate	8,7	13,3	8,4
Dioxane	58,9	66,7	54,6
Maleic acid	1,8	1,9	21,0
Methanol	4,4	4,8	0
Acetone	17,6	13,3	0
Cellulose acetate (CA 398-10)	8,6	0	8,4
Glacial acetic acid	0	0	7,6

Prior to testing for RO separations, membranes were annealed at temperatures ranging between the 70 and 100°C for 20-30 min. For testing, several membranes (3-4) were cut from a single large fabricated membrane. Testing was carried out at 2-3 MPa applied pressure with a 2000 ppm NaCl solution at pH 6 and 20°C.

2.4.3 RESULTS AND DISCUSSION

Only the best results recorded for each set of membranes are given here as there was a large scatter of results of the flat-sheet membranes; ascribed to the method of handmaking these membranes. The scatter of results of the single tubular membrane, made to date, was not nearly so great. A membrane sample of the Fastek module was also tested and results used with which to compare the IPS membranes.

Membrane test results are shown in Table 6.

TABLE 6:

RO performances of CTA and CA/CTA blend membranes compared to commercial CTA membrane . (Fastek)

Casting Solution	Annealing bath (°C)	Annealing bath (min)	Annealing batch Composition	Test pressure MPa	Salt Retention (%)	Flux (lmd)
Control Fastex membr. Flat-sheet membrane				2	97,7 ± 0,3	330 ± 6
F_1 (CA/CTA)	80	20	Distilled water	3	87,0	500
	80	20	Distilled water	2	83,4	277
	90	20	Ethyleneglycol 60% soln.	2	91,1	380
F_2 (CTA)	100	20	Distilled water + Ethyleneglycol 80% soln.	3	87,1	226
	80	30	Distilled water	3	72,6	365
	105	30	Ethyleneglycol 60% soln.	3	95,8	442
F_3 (CA/CTA)	80	20	Distilled water	3	94,9	208
	83	20	Distilled water	2	92,7	137
	84	20	Distilled water	2	93,8	140
	86	20	Distilled water	2	95,4	114
	75	20	Ethyleneglycol 50% soln.	2	97,5	117
Tubular membrane T_1 (F_2)	85	20	Distilled water	2	79,3	128

2.4.4 CONCLUSIONS

Flat-sheet and tubular RO membranes were successfully made from CTA and blends of CA and CTA. The large scatter of results observed for flat-sheet membranes was eliminated by making membranes by the mechanical tube-making process.

Use of aqueous ethyleneglycol solutions as annealing media gave membranes which had improved performance over these annealed in a pure water bath.

2.5 REMOVAL OF FOULANTS FROM MEMBRANE SURFACE

2.5.1 BACKGROUND

Although it was not a topic included in the initial program, it became necessary to establish effective and safe cleaning techniques for tubular cellulose acetate membranes. This was at the request of Membratek.

The effect which fouling has on the performance of RO membranes can, to a large extent, be counteracted by adopting regular cleaning procedures. The presence of organic or soft scale on membrane surfaces, in some circles regarded as a precursor for hard scale formation, generally leads to a deterioration in membrane performance. This is due to (i) increased resistance to hydraulic flow as well as (ii) an increase in osmotic pressure on the brine side of the membrane due to higher values of concentration polarization affected by the foulant layers.

Detergents are commonly used as a means to remove soft scalant layers of the organic type from RO membranes. When detergents are used to descale cellulose acetate (CA) membranes, care must be taken to ensure that the hydrolysis of the membrane is not accelerated by the high intrinsic pH levels of such detergents. CA hydrolyses and the rate of hydrolysis of CA is at a minimum at pH levels between 4 to 5, although RO plants are usually operated at pH levels between 5,5 to 6, as a trade-off between the cost of maintaining lower pH levels and the cost of membrane replacement due to hydrolysis at higher pH levels.

A study was conducted to establish "safe" operating pH levels for organic foulant removal.

It must be noted that alkaline solutions soften, swell and hydrolyze CA membranes. The softening phenomenon followed by recompaction at the higher operating pressures might mask initial deterioration in membrane performance, but repeated use of harsh cleaning procedures will eventually lead to permanent loss of membrane performance.

Base-catalyzed hydrolysis causes progressive deacetylation of CA and subsequent loss of permselectivity and mechanical properties of CA membranes. If hydrolysis takes place rapidly, permeability may increase owing to an increase in the number of hydrophilic hydroxyl groups **[10]**. If hydrolysis is a slow process, however, the increase in hydrophilicity may be overshadowed by increased compaction and accompanying loss of permeability, due to the fact that the hydrolyzed polymer is more readily plasticized by water.

Acid-catalyzed hydrolysis takes place at the chemical links which keeps the polymer backbone intact, breaking the polymer chain. The resultant loss in molecular mass leads first to a gradual deterioration in mechanical properties and ultimately to a loss in membrane integrity.

A summary only of the experiments carried out to ascertain the effects of various alkaline rinse solutions on the integrity of CA tubular membranes, and their results, will be given here. A more detailed report, including graphic represenations of results, is on record in an IPS in-house report **[11]**.

2.5.2 EXPERIMENTAL

Separate sets of membranes were treated in various ways, using the following conditions and for various periods of time as shown in Table 7.

TABLE 7:

Summary of experiments to study the removal of foulants from membrane surfaces

Control Study	Summary of Experiments
pH	NaCl RO followed by pH 8.0 [NaOH], not buffered. RO tap water rinses.
	NaCl RO followed by pH 10,4 [NaOH], not buffered, RO tap water rinses.
	NaCl RO followed by pH 8,5 [Borax/HCl buffered] RO tap water rinses.
	NaCl RO followed by pH 10,4 [Borax/NaOH buffered] RO tap water rinses.
Punch	NaCl RO followed by pH 8.0 Auto Punch [acidified with Sulphuric acid] rinses.
	NaCl RO followed by pH 8.5 Auto Punch [acidified with sulphuric acid] rinses.
	NaCl RO followed by standard pH 10,4 Auto Punch rinses.
Biotex	NaCl RO followed by pH 8,5 Biotex [acidified with sulphuric acid] rinses.
	NaCl RO followed by pH 9.2 standard Biotex rinses.
The feed pressure was maintained at 2 000 kPa through-out the exercise, except during RO tap water/NaCl feed solution replacements.	

2.5.3 RESULTS AND DISCUSSION

Membranes were subsequently tested for their salt rejection and flux. The A^2/B value **[12]** (the measure of the overall membrane performance used to compare membranes with different rejection and flux values) was also calculated for each membrane. Results were presented graphically **[11]**.

It was found that the pH 10,4 solutions had a deleterious effect on the performance of the membranes and should not be used.

A decline in membrane performance, over the test periods, in the case of all the other alkaline rinse solutions was also evident from the results. However, the initial membrane performances seemed to be restored after a period of operation under standard operating conditions, even in the case of pH 9,2 Biotex.

No conclusions could yet be made regarding the combined pH effect of alkaline rinse solutions in the presence of iron foulant layers, since the test equipment used is devoid of any such foulants.

The tubular membrane configuration lends itself to cleaning by mechanical means; this can be used in conjunction with moderately alkaline detergent washes. This is an advantage which the spiral wrap and hollow-fine systems do not have. Flow reversal, per *se*, as well as flow-reversal in conjunction with foam-ball swabbing and/or compressed air introduction during detergent washing cycles will improve the effectiveness of any detergent.

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3. IMPROVEMENT OF POLYETHERSULPHONE (PES) UTF MEMBRANE TECHNOLOGY

3.1 ROLE OF VARIOUS SUPPORT FABRICS IN MEMBRANE MORPHOLOGY AND INTEGRITY

To date, these has not been a need for any changes to be made in the existing technology which is considered to be adequate.

3.2 MODIFICATION OF CASTING SYSTEMS/ENVIRONMENT TO CREATE RANGE OF PRODUCTS

3.2.1 BACKGROUND

During the first meeting of the applications sub-committee for the current project "Development of fixed and dynamic membrane systems for the treatment of effluents and brackwater by MF, UF and RO processes", held at Megawatt Park on 31 July 1989, the requirements of the water industry for the application of membrane technology were extensively discussed and several identified. A non-PES membrane, having a molecular mass cut-off of 800-1200 (a NF membrane) and which would not be fould by lignans was required by the paper and pulp industry; it would be used to remove colour from effluents, concentrate lignans and be used for general effluent water treatment. In the textile industry, UF applications existed for membranes with 10 000-20 000 cut-off. Serious oil-fouling problems were encountered in this area.

It was decided that various different membranes should be tested in the industrial situation. SASOL was able to offer suitable effluents for evaluation of membranes: these effluents had a high salt content and were generally representative of the typical contaminants encountered by other industries.

These two goals put increased priority on the development of the non-nitrogen-containing polyvinyl alcohol membrane (see section 5) and even stronger emphasis on the development of a low cut-off ultrafiltration membrane. (There was subsequently therefore a hold placed on the development of thermal inversion membranes and a lower priority placed on capillary membranes.)

This priority change proposed by the sub-committee was aimed at attaining technology transfer to Membratek in the near future. Membratek already posses the production plant and module production facilities to immediately implement low cut-off UF technology.

3.2.2 RESULTS AND DISCUSSION

Development of the manufacture of low cut-off UF PES membranes by IPS was soon achieved and technical transfer was subsequently accepted by Membratek. The relevant technical transfer document "Development and transfer of technology for the manufacture of low cut-off ultrafiltration membranes" was drawn up by Ed Jacobs and Heinz Ströhwald (May 1991) and submitted to the WRC. This document describes the techniques for implementation of such membranes in inudstry; the latter carried out as a separate programme by Membratek.

The following summarizes the document; and includes highlights of membrane performances.

The development of low molecular-mass cut-off ultrafiltration membranes was carried out at the Institute for Polymer Science by the variation of some of the fabrication parameters known to influence membrane productivity and retention (polymer concentration, air-drying, temperature, casting solution formulations, glycerol, post-treatment).

The performance of the membranes that were produced in the laboratory could be duplicated on commercial membrane manufacturing equipment after adaptation of the polymer solution formulations, while accepting the differences in certain production conditions. The objective was to produce membranes with an acceptable performance using the manufacturing equipment of Membratek and not to merely duplicate laboratory conditions. As a result three types of low-molecular-mass cut-off (MMCO) ultrafiltration membranes were developed (M460, M441, M442) with performance characteristics comparable to, and often better than, similar commercial membranes made by Wafilin. Typical results of RO performances of some Membratek produced low MMCO PES UF membranes are shown in Table 8. Evidence was found of sharp pore-size distribution, in particular in membrane type M433.

As such it is evident that the objective of the technology transfer, to produce low MMCO UF membranes commercially, had been accomplished.

The newly developed membranes showed economical productivity and useful retention characteristics in application studies concerning colour removal from natural waters and process streams of the sugar industry.

The second objective of producing low MMCO membranes which are useful in commercial applications was therefore also met.

TABLE 8:

Pure water flux and UF flux and retention performances of some Membratek-produced low MMCO PES UF membranes

		Molecular Mass PEG			
		17K		6K	
Membrane code	PWF (lmh)	Flux (lmh)	Retention (%)	Flux (lmh)	Retention (%)
M440 (433)					
200 kPa	39,3	35,3	99,3	26,5	97,1
500 kPa	137,2	56,4	91,3	71,3	83,9
M441 (431)					
200 kPa	58,3	38,6	99,2	49,0	97,5
500 kPa	174,3	57,2	87,0	86,4	84,4
M442 (437)					
200 kPa	96,7	43,7	98,6	56,3	98,4
500 kPa	251,4	57,7	86,2	87,6	89,9

UF test conditions: 1,5 m/s; 200 kPa; 20°C; 0,5 mass% solids
PWF at pressures indicated, 20°C

3.3 CHARGED UF MEMBRANES

Such a study was not carried out during this contract period.

3.4 MODULE DESIGN

See Aim 4, section 7.

3.5 CLEANING REGIMES

Cleaning of PES UF modules has been well described by Membratek. The only problems which have been encountered to date include the selection and use of enzymes for specific effluents and the problem of hydrolytic resistance of the support fabric.

To ensure minimum operating downtime with the highest throughflow of permeate, cleaning techniques need to be optimized for each application. This work is therefore ongoing.

3.6 POST-TREATMENT OF PES UF MEMBRANES

Although the post-treatment of membranes was not one of the original aims of this project, circumstances led to the search for effect post-treatment procedures. During transport of membranes, problems arose due to module leakage at the inlet-outlet or permeate inlet or outlet ports.

A similar problem could arise with the MEMTUF open membrane system. Once the PES membranes dried out, they densified, leading to a decrease in membrane performance. A programme was initiated for the post-treatment of PES UF membranes to prevent deterioration of the membranes as a result of densification when stood in the open.

3.6.1 BACKGROUND

Wet phase-inversion is most commonly used to produce membranes with an asymmetric structure. In short, the method requires that a thin film, spread from a membrane-casting solution, is brought into direct contact with a non-solvent coagulant. The general rule is that all solvents and non-solvent additives used in the make-up of the casting solution must be miscible in all proportions with the non-solvent coagulant-system used.

The surface of the membrane film gels immediately upon contact with the coagulant, forming the finer mazed dense, skin-section. Liquid-liquid phase-separation of the remaining nascent polymer film results from the diffusion, mixing and exchange of the coagulant with the solvent-system of the membrane-forming polymer across the skin-layer interface.

By a mechanism of nucleation and growth the solution separates into two phases, one polymer-rich and the other solvent-rich. Gelation occurs when the polymer-rich phase reaches certain threshold viscosity limits. In the final membrane the polymer-rich phase forms the continuous phase, whereas the interdispersed discontinuous solvent-rich phase gives rise to its characteristic porous structure. Water is commonly used as a bulk constituent of the non-solvent coagulant, and although additives are used to generate certain properties (e.g. surfactants to enhance re-wettability, etc.), these are used in relatively small proportions.

A problem which often arises with asymmetric membranes is that they lose their original performance characteristics when allowed to dry out completely. Most of these membranes therefore need to be stored wet, either immersed in water, or in a 100% relative humidity atmosphere to prevent water from diffusing from the membrane structure.

Even in the case of relatively hydrophobic membrane-forming polymers such as poly(bisphenol-A sulphone) (PS) and poly(arylether sulphone) (PES), water is well interdispersed with the polymer-network of the membrane matrix. However, when these relatively hydrophobic polymers lose the water contained within their matrices, the membrane structure not only shrinks and densifies, but it also becomes extremely difficult to rewet the membrane to its original water content. Certain threshold pressures therefore commonly occur below which no water will permeate a completely dried membrane. The retention performance of such membranes also differs drastically from that of the original membrane.

When PES membranes are epoxy-cast into modules, or transported, it is sometimes difficult to maintain an atmosphere of relative high humidity throughout the operation. A method therefore needed to be developed to extend the open-air storage-time of tubular PES membrane elements.

3.6.2 EXPERIMENTAL METHODS

Membrane fabrication

A continuous process was used for the production of the support tube and simultaneous extrusion of the membrane film. In all cases referred to in the text the membranes were introduced continuously and directly into the coagulation medium; the membranes therefore were not subjected to an intermediate air conditioning step before coagulation.

Various membranes were produced from different casting solution compositions (see Table 9) and under different casting condtions. Table 10 shows some of the more important fabrication conditions,

TABLE 9:
Selected casting solution formulations for tubular membranes, to be post-treated

Membrane code	PES	NMP	DMF	DMAc	PVP^{30}	PVP^{10}	LiCl	PEG^{400}
516/719	19,0	68,8	2,0		10,0		0,2	
519/719	19,0	68,8	2,0		10,0		0,2	
526/719	19,0	68,8	2,0		10,0		0,2	
517/339	22,0	68,0			10,0			
518/334	18,0	77,0			5,0			
520/337/10	22,0			73,0	5,0			
520/337/15	22,0			73,0	5,0			
520/337/20	22,0			73,0	5,0			
521/342	22,0			73,0		5,0		
523/341	22,0			68,0	10,0			
524/341	22,0			68,0	10,0			
525/341	22,0			68,0	10,0			
527/333	20,0	58,0			20,0			2,0
528/723	26,0	53,9		14,7	3,5	1,5	0,4	

DMAc	N-N, dimethyl acetamide	PEG400	Polyethylene glycol
DMF	N-N, dimethyl formamide	PES	Victrex P200
LiCl	Lithium chloride	PVP10	Luviskol 30, polyvinyl pyrrolidone
NMP	N-Methyl pyrrolidone	PVP30	Kollidon 30, polyvinyl pyrrolidone

TABLE 10:

Selected membrane fabrication conditions
(for membranes listed in Table 9)

Settings/Trial No.	516	517	518	519	520	521	523	524	525	526	527	528
Air gap height	300	300	300	300	150	150	150	150	150	150	150	150
Mandrel design	#4	#4	#4	#4	#4	#4	#4	#4	#4	#4	#4	#4
Cavity pressure	130	130	130	130	0	0	100	110	110	110	110	110
Vacuum assisted	No	No	No	No	No	No	On	On	On	On	On	On
Cast speed	3,7	3,6	3,7	3,7	3,7	3,7	2,6	2,6	3,7	2,6	2,6	3,7
Coagulant additives	No	No	No	No	X100	X100	NaCl	No	No	X-100	X-100	X-100
Coagulation temp.	19,4	18,7	20	22,5	2020/15/10		15	20	20	18,4	20	16,7
Rowrate air	0	0	0	0	0	0	1,2	1,2	1,2	1,2	1,2	1,2

Membrane storage

The normal procedure followed after membrane fabrication, was to store the membranes in shallow flat tanks which were flushed with RO tap water at regular intervals. The tanks were maintained clean of microbial growth by adding shock dosages of chlorine to the tanks at once-a-week intervals. Samples of these wet-stored membranes, taken for control evaluation purposes, are referred to as 'wet-stored' control membranes.

Membrane conditioning

Membrane samples of 500 mm lengths were randomly selected from each of the different production batches for conditioning in unstirred glass tanks filled with the appropriate concentrations of mono-ethylene glycol (industrial grade) or glycerol (industrial grade) in water. Formaldehyde (0,5 mass percent) was added to the glycerol conditioning-tanks to prevent microbial growth.

The conditioning baths were kept in an air-conditioned room (20°C). An electrical heat-circulator was used to maintain the conditioning baths at elevated temperatures when required. After being conditioned, the membranes were drained vertically for 24 h and then stored open, on racks, in a temperature- (20°C) and relative humidity- (50%) controlled room.

Membrane evaluation

All membranes were evaluated for their initial pure water flux performance, a test which was conducted at a feed pressure of 200 kPa, a linear-flow velocity of 0,5 m/s, a feed temperature of 20°C, with RO tap water as the feed.

All the membranes were also subjected to an ultrafiltration test, in which their ability to retain an approximately 40 000 molecular mass polyvinylpyrollidone (Kollidon 30, BASF)(PVP30) was determined. An 0,5 mass percent solution of the PVP30 in RO tap water was used as the feed solution. The UF test loop was operated at an inlet pressure of 500 kPa, a feed temperature of 20°C, while the inlet linear flow velocity was maintained at 1,2 m/s.

The solute retention performance of the membranes was determined gravimetrically. Samples (50 ml) of both the feed and permeate solutions were evaporated to complete dryness at 50°C in a circulating oven. The capability of the membrane to retain the solute was determined gravimetrically as the difference between the dry solute mass of the feed and permeate samples, expressed as a percentage of the dry solute mass of the feed sample.

3.6.3 RESULTS

Table 11 shows the PWF and UF performances of the wet-stored control membranes. Six 400 mm x 13 mm diameter tubular membrane test sections were evaluated in each test, and the results shown in the Tables are the mathematical averages of their individual rates of permeation and retention performances.

TABLE 11:
Pure water flux and UF performance of PES UF membranes

Membrane Code	Pure Water Flux Flux [lmd]	UF performance Flux [lmd]	Rejection [%]
527/333	6 500	1 200	69,7
518/334	22 000	1 200	70,6
520/337	21 300	1 300	62,4
517/339	3 400	1 100	81,1
523/341	7 400	1 300	68,4
524/341	8 700	1 200	61,5
525/341	8 200	1 400	68,6
521/342/10	16 600	1 100	75,8
521/342/15	18 200	1 300	72,2
521/342/20	22 700	1 500	61,5
516/719	12 200	1 100	81,9
519/719	11 200	1 200	67,9
526/719	12 400	1 400	62,2
528/723	670	1 000	83.3

Table 12 shows how the UF performances of 516/719-series membranes changed when the membranes were allowed to dry under the conditions shown .

TABLE 12:

The effect of modification of membrane surface properties, in a post-treatment step, on RO performance

516/719-Membranes conditioned in an aqueous ethylene glycol solution for 24 h			
Mass Percent Ethylene glycol in conditioning tank	Dry-store 3 days (20°C) lmd/%	Bake 20 min at 80°C Test directly lmd/%	Bake 20 min at 80°C Dry-store 3 days (20°C) lmd/%
Untreated/Wet-Control	38/97,5	140/94,6	49/99,3
Treated			
20	1 050/89,4	110/94,4	570/86,4
40	1 100/83,3	700/81,1	740/80,2
60	1 100/82,5	940/73,5	950/75,5
80	1 140/77,7	1 000/73,0	940/77,8

The rates of water permeation of all the membranes show a marked increase above that of the untreated dried out, wet-control membrane, which was exposed to identical drying-out conditions as those of the treated membranes.

An interesting phenomenon is noted when the performances of the thermally treated conditioned membranes (last two columns of Table 12) are compared. Stress-relaxation in the skin-section of the membranes which had stood for three days before being tested, enhanced by the plasticizing effect of the ethylene glycol, is the most probable explanation for the difference in retention and flux behaviour of these membranes when compared with that of the similarly treated but directly tested membranes.

The effect which increased ethylene glycol concentration has on the water permeation rates and on the retention performances of the treated dry-stored membranes is also noticeable. The plasticizing effect of the 80% ethylene glycol treatment enhances relaxation in the stressed membrane skin, causing an increase in the average membrane pore diameter, with a resulting reduction in the retention of PVP.

Table 13 shows the RO performance results of a number of differently produced membranes.

TABLE 13:

Open-kept membranes - the effect of post-treatment on the RO performance of some PES UF membranes

Membrane Code	Wet-stored		24 h/20°C Treatment 1:1 EG*/Water Store open, 20°C		24 h/20°C Treatment 1:1 Glycerol/Water Store open, 20°C		Annealing 1:1 EG*/Water Store open, 20°C	
	Storage time (days)	Flux/Rej	Storage time (days)	Flux/Rej	Storage time (days)	Flux/Rej	Storage time (days)	Flux/Rej
527/333	1	1160/69,7	4	1300/71,6	10	1300/69,2		
			17	1240/78,0	16	1150/73,2		
526/719	6	1380/62,2	12	1340/60,6	7	1370/62,3		
					25	1120/67,1		
528/723	2	1040/83,3	7	930/85,2				
523/341	5	1300/68,4	7	1300/73,0				
			26	314/89,1				
524/341	5	1200/61,5	7	1770/54,6				
			13	1160/68,4				
525/341	5	1350/68,6	8	1680/55,6				
520/337	3	1250/62,5	4	1110/72,4			4	[a]1100/70,7
	14	1600/63,7	28	1020/74,6			24	880/72,8
521/342/10	4	1090/75,8	7	1540/78.2			4	[b]1220/78,4
	11	1100/75,6	19	1000/90,5			18	980/85,0
521/342/15	3	1290/72,2	4	1200/76,8			3	[c]1500/64,2
			14	970/83,2			14	1140/82,7
521/342/20	3	1500/61,8	6	1300/69,4			6	[b]1340/73,6
	12	1130/73,7	21	1050/73.2			20	1060/69,3
519/719	7	1180/67,9						
	66	1200/69,7						
518/334	11	1200/70.6						
	28	1180/67,2						
517/339	9	1070/81,1	0	1270/80.6			1	[b]1130/80,1
	43	1180/77,6	31	940/86,8			32	1100/79,2

Note: Annealing conditions: a) 20 Minutes at 80°C. b) 30 Minutes at 50°C, c) 40 Minutes at 80°C

Note: (Days) - Membrane evaluated after storage for x-number of days at given conditions

* EG - Ethyleneglycol

When these results are compared, it is evident that no dramatic loss of membrane permeability occurred, as would have resulted when untreated membranes were allowed to dry out completely over a three-day period. In general, the treated dry-stored membranes exhibited higher average retention performances than the wet-stored control membranes did. This could have been due to a slight densification of the membrane skin structure which resulted from some evaporative loss of water.

The effect which coagulant temperature has on the retention performance of UF membranes is clearly seen when the performances for the 520/342-series membranes are compared. As the temperure of the coagulant was increased in steps of 5°C from 10°C up to 20°C, the average pore diameter of the resulting membranes increased, which in turn led to lower solute retention and higher permeate flux rates. A marked increase in the retention of the 521/342/10 membrane was observed, when compared with the wet-stored control, when the treated membrane was stored open for a 19-day period.

3.6.4 CONCLUSIONS

The conclusions which can be drawn from this work are (i) Catastrophic loss in the low-pressure performance of dry-stored PES UF membranes can be prevented or delayed if the membranes are treated in aqueous solutions of either mono ethylene glycol or glycerol, and (ii) this post-treatment may also be used to alter the performances of the membranes, and therefore used as a post-treatment step.

4. ULTRATHIN FILM (UTF) REVERSE OSMOSIS (RO) POLY-2-VINYLIMIDAZOLINE (PVAM) MEMBRNES

4.1 BACKGROUND

Early research into thin-film composite PVAM RO membranes, in flat-sheet form, and consideration of the numerous fabrication variables of such membranes was carried out during the previous contract period programme. Good results were obtained from early membranes, a selection of which is shown below, and this led to the expansion of the research in this field, and making of PVAM membranes in tubular form.

TABLE 14:

RO performance of a selection of early flat-sheet PVAM UTF RO membranes

Crosslinking agent for PVAM	Fabrication procedure features	RO performance	
		Salt rejection (%)	Flux (lmd)
IPC	low MM PVAM	72,7 ± 0,4	1760 ± 58
IPC	high MM PVAM	62.5 ± 4,8	2174 ± 235
SCl	low MM PVAM	84,8 ± 1,9	680 ± 58
SCl	high MM PVAM	86,1 ± 3,0	851 ± 65
Cl2S	low MM PVAM.OTEA	96,4 ± 0,6	797 ± 86
	+ TEA	96,2 ± 0,6	1394 ± 50
Cl2S	high MM PVAM.OTEA	93,9 ± 1,8	1394 ± 50
	+ TEA	93,7 ± 1,8	1444 ± 50
Above membranes tested at 4 MPa with 5000 ppm NaCl at 25°C			
SCl	medium MM PVAM/0 piperazine	92,8 ± 0,7	272 ± 67
SCl	+ piperazine	92,8 ± 0,9	398 ± 101
Cl2S	+ piperazine	94,4 ± 0,4	1030 ± 40
Above membranes tested at 2 MPa with 2000 ppm NaCl at 25°C			

During the current contract period, emphasis was placed on the making of tubular UTF composite PVAM membranes, their optimization for rejection and flux, and transfer of composite membrane technology to Membratek. On the chemical side, characterization of the copolymeric PVAM material, by sophisticated ^{13}C NMR analytical techniques was to be investigated; a method was subsequently developed by which the quality of different batches of PVAM could be ascertained. Model compound studies were begun in an attempt to determine, on a molecular level, the stability of PVAM membranes in harsh environments (high and low pH and chlorine).

4.2 RESULTS AND DISCUSSION

During the term of the present contract period, the following tasks were completed:

- PVAM/SCl membranes were successfully made in tubular form by a semi-automated process, (and found to have better RO performances than the flat-sheet membranes);
- The design of production equipment for making 3 m PVAM/SCl composite membranes was finalized;
- Reaction conditions for the fabrication of PVAM/SCl tubular membranes were optimized for high retention and flux by means of the mathematical simplex approach.

Details pertaining to these above points have been given in the Ph.D.-thesis of E.P. Jacobs [1].

- A large supply of membrane chemicals was made and stored until required;

- A quality control method for different batches of PVAM was developed, using high resolution ^{13}C NMR spectroscopy.

Details of the above two points are included in the Ph.D.-thesis of M. Hurndall "The Chemistry of Poly-2-vinylimidazoline RO membranes" (thesis in preparation).

The mathematically optimized fabrication conditions and the resulting RO performances of PVAM/SCl membranes are shown here in Tables 15 and 16. (Two different PVAM precursors used, separately.)

TABLE 15:

Optimized PVI I tubular membrane fabrication formulation and RO performance

Concentration of PVI I precursor	[mass %]	5,0
Concentration of triethylamine	[mass %]	1,1
Concentration of trisodiumphosphate	[mass %]	0,14
Precursor contact time	[min]	43,00
Precursor draining time	[min]	1,50
Concentration crosslinking agent: 3-(chlorosulphonyl)benzoyl chloride	[mass %]	4,50
Crosslink reagent contact time	[min]	3,00
Post-crosslink air drying time	[min]	10,00
Oven temperature	[°C]	95,00
Oven residence time	[min]	5,40
RO performance	Salt Retention	97,1 ± 0,1%
	Permeate flux	730 ± 24,1 lmd
	A^2/B value	8,89 x 10^{-5}

TABLE 16:

Optimized PVI II tubular membrane fabrication formulation and RO performance

Concentration of PVI II precursor (batch 3)	[mass %]	1,2
Concentration of triethylamine	[mass %]	0,2
Concentration of trisodiumphosphate	[mass %]	0,5
Precursor contact time	[min]	15,0
Precursor draining time	[min]	4,0
Concentration crosslinking agent: 3-(chlorosulphonyl)benzoyl chloride	[mass %]	3,0
Crosslink reagent contact time	[min]	6,0
Post-crosslink air drying time	[min]	16.00
Oven temperature	[°C]	95.00
Oven residence time	[min]	4.0
RO performance	Salt Retention	98,2 ± 0,7%
	Permeate flux	560 ± 150 lmd
	A^2/B value	10,9 x 10^{-5}

Two sets of membranes were subsequently made with PVI III precursor (a "purified" material) and crosslinked with 3-(chlorosulphonyl)benzoyl chloride. These membranes were made under the optimized fabrication conditions established for the PVI I and the PVI II membranes (see Tables 15 and 16), and their RO performances are compared. Results are presented in Table 17.

TABLE 17:

RO performances of tubular membranes made with precursors PVI I, PVI II or PVI III and crosslinked with SCI

Fabrication formulation	Polymeric precursor	RO performance Salt retention [%]	 Flux [lmh]
Optimum for PVI I/SCI membranes	PVI I PVI II PVI III	97,4 ± 0,5 62.6 ± 15,0 80,3 ± 6,1	12,3 ± 0,2 1,0 ± 0,2 1,0 ± 0,2
Optimum for PVI II/SCI membranes	PVI I PVI II PVI III	94,5 ± 0,3 97,4 ± 1,6 97,0 ± 1,1	20,4 ± 1,4 17,4 ± 1,7 26,8 ± 3,1

Membranes prepared with the PVI III precursor, using the optimum formulation for PVI II membranes, were considered to showed the best performance.

Membranes were tested with chlorinated feedwater and, as with all other N-containing membranes, they were found to be not resistant to chlorine. The salt-retention of PVAM/SCI tubular membranes decreased within 200 h of exposure to feed solutions containing about 5 ppm free chlorine at pH 5,6 and pH 8,0.

The deterioration was less severe for a feed solution containing up to 6 ppm free chlorine at pH 6,6. These membranes were threfore more chlorine tolerant than the early overseas membranes made from PEI **[3]**, but not as stable as the Film Tec membranes [4].

Acid conditions also had a detremental effect or the salt rejection performance of the PVAM/SCI membranes. The optimum pH range for operating these membranes was about 5,5 - 7,5, seen from Figure 2.

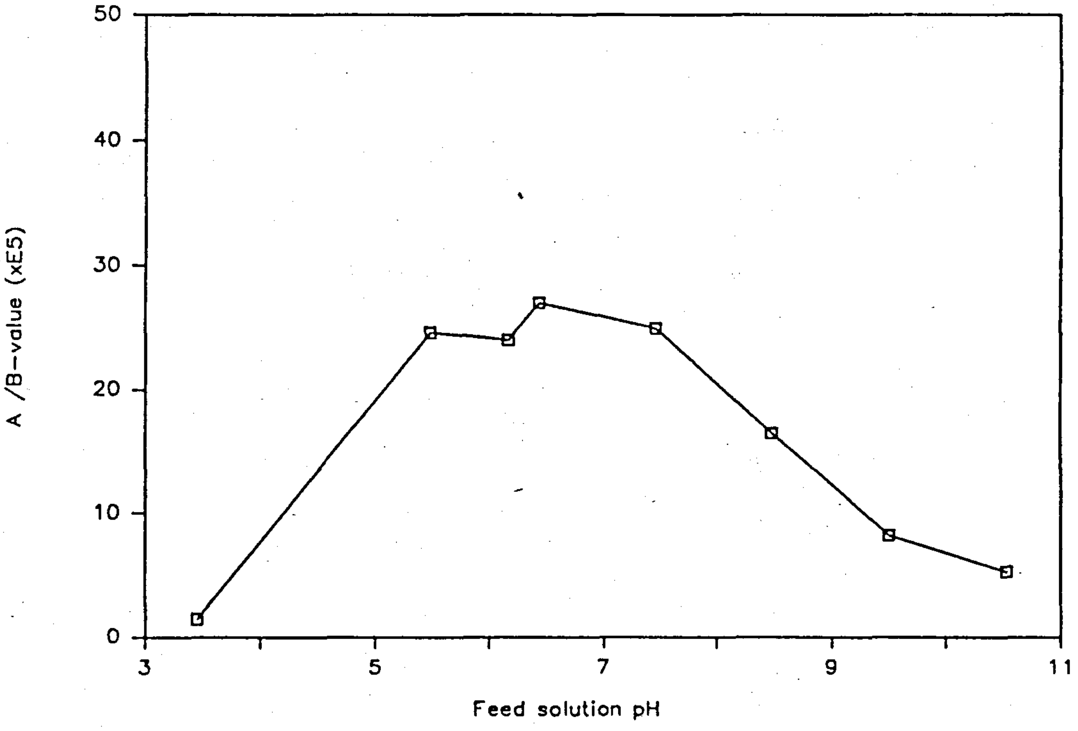


FIGURE 2:
RO performance of PVAM/SCl membranes vs pH feed solution

During the period of this contract, it appeared that there was not a market for UTF composite tubular membranes. (There had also been no market for the Film Tec tubular-technology membranes from PCI, for which Membratek had the agency.)

SECTION 2:

5. NON-NITROGEN-CONTAINING UTF RO MEMBRANES

5.1 BACKGROUND

This programme was initiated to develop nanofiltration and RO membranes which could have the following possibilities:

- Replace cellulose diacetate membranes for certain applications;
- Offer membranes with properties that could create new applications;
- Make membranes more tolerant that could create new applications.

These requirements for membranes emerged from the Application Sub-Committee meeting held at Megawatt Park, July 1989 (see also section). Aspects discussed at this meeting included Mr. Botha's request for a hydrophilic membrane with a rejection of 93 to 95% and working at low pressure, Mr. Spencer's mention that fouling is important and saying that they would prefer a chlorine-resistant membrane which is "operator-friendly", Mr. Breyer-Menke's referring to AECI's need that they would prefer a membrane which is reliable, easy to clean and robust, and Mr. Botha's addition that a robust membrane should resist surfactants, mineral oils, organic solvents, oxidants and changes in pH.

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

During an overseas visit, we had contact with the head of Filmtec research establishment (Dr. Koo) who also explained that there is world-needed for an operating friendly membrane and that this was also an aim of the Dow and Filmtec companies. Nitto Denko in Japan had recently achieved very good results with a polyvinylalcohol-based membrane; 60 to 70 NaCl rejection for brackwater at moderate operating pressure. Later, a second polyvinylalcohol-based membrane, the Filmtec 70, become commercially available. This was a nanofiltration membrane offering 5% sodium chloride rejection from dilute brackwaters.

An extensive literature survey into PVOH and PVOH-based membranes was therefore undertaken. Several industrial patents relating to the latter were found.

During the contract period two main avenues of use of PVOH were subsequently followed. Firstly, PVOH was incorporated into the known PVAM UTF RO composite membranes (N-containing membranes) in an attempt to achieve increase fluxes without too much loss in rejection.

Seconly, the making of membranes from hydroxyl-containing polymers (e.g. PVOH) and copolymers as membrane materials was investigated. Selected PVOH-containing copolymers, previously used for making dynamic membranes, were also used, in a new way: to make UTF membranes which would operate at very low pressure and still exhibit reasonable fluxes.

5.2 LITERATURE SURVEY

A detailed literature survey covering non-nitrogen-containing UTF RO membranes, with emphasis on the use of crosslinked PVOH as a membrane material, is on file at IPS **[1]**. Much of the literature focused on the crosslinking reaction of PVOH and on PVOH-based RO membranes. It was found that the interfacial polymerization of multifunctional hydroxyl compounds had, to date, not received much attention in the area of RO membrane development.

In the preparation of chlorine-resistant PVOH-based membranes for low-pressure desalination of brackish water and industrial wastewater, the most successful approach, to date, has been that of preparing thin-film composite membranes comprising (i) a porous substrate, (ii) an ultrathin salt-retention barrier formed by interfacial cross-linking and polymerization of PVOH and an amino compound having at least two secondary amino groups with a multifunctional reagent that reacts with the secondary amino groups and the hydroxyl groups of PVOH, and (iii) an inner layer of water-insoluble PVOH that is present between the porous substrate and the ultra-thin film. This procedure, developed by Nitto Electric Industrial Co. in Japan, has been described extensively in the patent literature **[2-4]**.

Typically, a porous polysulphone support is coated with an aqueous solution of PVOH, piperazine, and NaOH as acid acceptor, then dipped into a hexane solution of trimesoyl chloride, dried, and heat-treated at 110°C. In a slight variation of this procedure, aromatic diamines, e.g., m-phenylene diamine, are used instead of cycloaliphatic secondary diamines **[5]**. A similar approach has been followed by researchers at Sumitomo Chemical Co. **[6]**, but they used poly(ethylene glycols) and other polyhydroxy compounds instead of PVOH.

The RO performance of Nitto's NTR-7250 chlorine-resistant membranes in brackish water desalination applications has been discussed by Kamiyama et al. **[7]**. These thin-film composite PVOH-based membranes exhibited high $MgSO_4$ retentions, but low NaCl retentions. After the NTR-7250, Nitto developed the NTR-729 and NTR-739 HF (high-flux) series membranes [8, 9]. These are thin-film composites made from modified PVOH. They exhibit excellent chlorine resistance, high water flux, and high NaCl retention in brackish water desalination, even at low pressures of 1 MPa.

5.3 INCORPORATION OF PVOH INTO PVAM MEMBRANES

5.3.1 BACKGROUND

UTF composite membranes had been successfully made from PVAM crosslinked with 3,5-dichlorosulphonylchloride (see section 4).

Prompted by the request from Membratek for a nanofiltration membrane, and making use of the known technology of making PVAM membranes. Polyvinyl alcohol was blended into the polymeric precursor used in the making of the known PVAM composite membranes. This produced lower salt-rejection low-pressure membranes.

5.3.2 EXPERIMENTAL

Membrane fabrication conditions for the making of the PVAM + PVOH/SCl UTF membranes are given in Table 19.

TABLE 19:

Poly(vinyl alcohol) filled PVAM UTF membranes. Membrane fabrication conditions

Precursor solut. composition (mm %)	CAM	CAMOH 2	CAMOH 3	CAMOH 4	CAMOH 5	CAMOH 6
PVAM II	1,2	1,14	1,08	1,02	0,96	0,60
PVOH^a	0	0,06	0,12	0,18	0,24	0,60
TEA^b	0,2	0,2	0,2	0,2	0,2	0,2
TSP^c	0,5	0,5	0,5	0,5	0,5	0,5
SCl crosslinking agent; 3,5 mass %						
Oven temperature (°C)	95					
Oven time (min)	5					
Wetting and draining times (min)						
Substrate predraining	10					
Precursor contact time	15					
Precursor draining time	8					
Crosslink contact time	6					
Crosslink draining time	16					

a PVOH Poly(vinyl alcohol) mol mass 72 000
b TEA triethylamine
c TSP trisodiumphosphate

Membrane fabrication conditions for the making of PVAM-C + PVOH/SCI UTF membranes are given in Table 20.

TABLE 20:

Membrane fabrication conditions of PVAM-C/SCI membranes, filled with AHEA-1 or PVOH

Precursor solution composition (mm %)	CAM 5	CAM 6	CAM 7	CAM 8	CAM 9	CAM 10	CAM 11
PVAM-C precursor	1,2%	0,96	0,96	0,96	0,96	0.96	0,96
AHEA-1				0,24	0,24	0.24	
PVOH (72K, 86%)		0,24	0,24				0,22
PDA							0,09
TEA		0,2	0,2	0,2	0.2	0,2	0,02
TSP		0,5	0,5	0,5	0,5	0,5	0,5
SCI crosslinking agent: 3,5 % mass							
Oven drying							
Oven Temp. (°C)	95	95	115	95	105	115	95
Oven Time (min)	5	5	5	5	5	5	5

Fixed wetting and draining time (min)	
Substrate predraining	10
Precursor contact time	15
Precursor draining time	8
Crosslink contact time	6
Crosslink draining time	16

The synthesis of PVAM, PVAM-C and the crosslinking agent SCI are described in detail in a Ph.D. thesis, in preparation **[10]**.

5.3.3 RESULTS AND DISCUSSION

Membranes fabricated from a precursor solution containing PVAM (PVAM II, isolated by freeze-drying) and PVOH (in concentrations of up to 0,25%) gave membrane with significantly higher fluxes albeit with slightly lower salt-rejections than the control PVAM membranes. The effect of PVOH as additive to a PVAM precursor solution on the RO performance of membranes is shown in Figure 3.

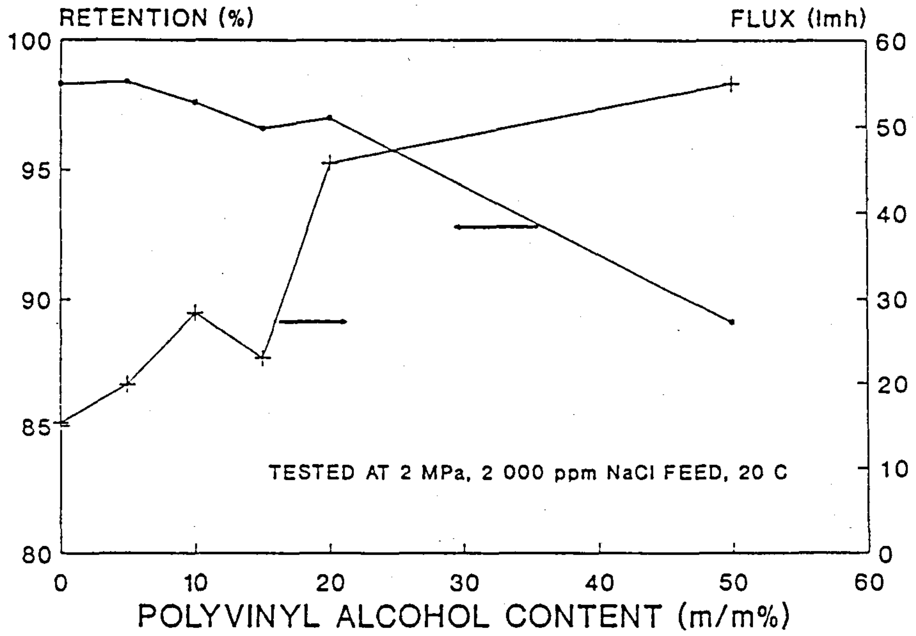


FIGURE 3:
The effect of the addition of PVOH to the precursor solution on the RO performance of modified PVAM II/SCI tubular membranes

It is seen that the addition of PVOH leads to increased fluxes. Two membranes were tested for an extended period, with a PVAM II/SCI membrane as control (PVI). Results are shown in Figure 4. The membrane filled with PVOH showed a slight increase in retention with time whereas the control PVAM membranes showed practically no improvement in performance.

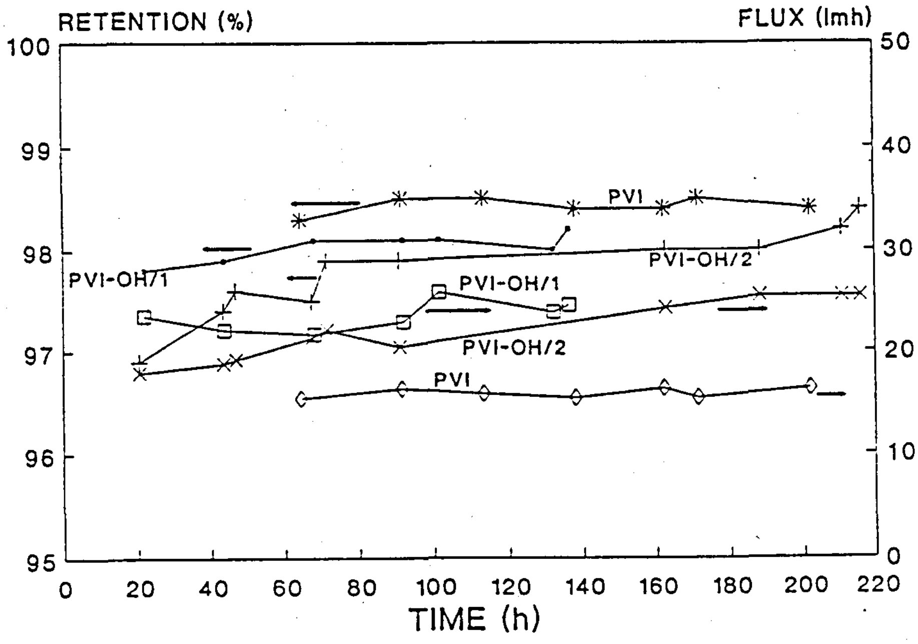


FIGURE 4:
The effect of time on the RO performance of PVAM and PVOH-modified-PVAM membranes (PVI-OH/1 and PVI -OH/2) respectively. PVOH addition was 20% (m/m %)

As the concentration of PVOH in an aqueous PVAM precursor solution was increased, there was a drastic increase (about three-fold) in the resultant membrane flux, although at the cost of a reduction in the membrane's salt retention. Whereas a 20% PVOH content gave membranes which showed only a slight decrease in retention (< 2%), a 50% PVOH content gave membranes which had their retention reduced by up to 10%.

It had been established that membranes which were fabricated from the PVAM-C precursor (PVAM from which excess ethylenediamine had been removed by solvent extraction and which contained about half the quantity of ethylenediamine as did the PVAM precursor itself), gave better RO performance results than the PVAM membranes, prepared according to their optimum formulation. In the continued search for membranes with the abovementioned type of performance (adequate RO performance at low operating pressures) membranes were fabricated from precursor solutions containing PVAM-C and PVOH (and, in cases, AHEA-1). The RO performances of these membranes, together with a control PVAM membrane (CAM 5), were recorded at different operating pressures and also over an extended period of time (200 h), with a 2 000 mg/ℓ NaCl solution at 20°C. Results are shown in Figures 5 and 6 respectively.

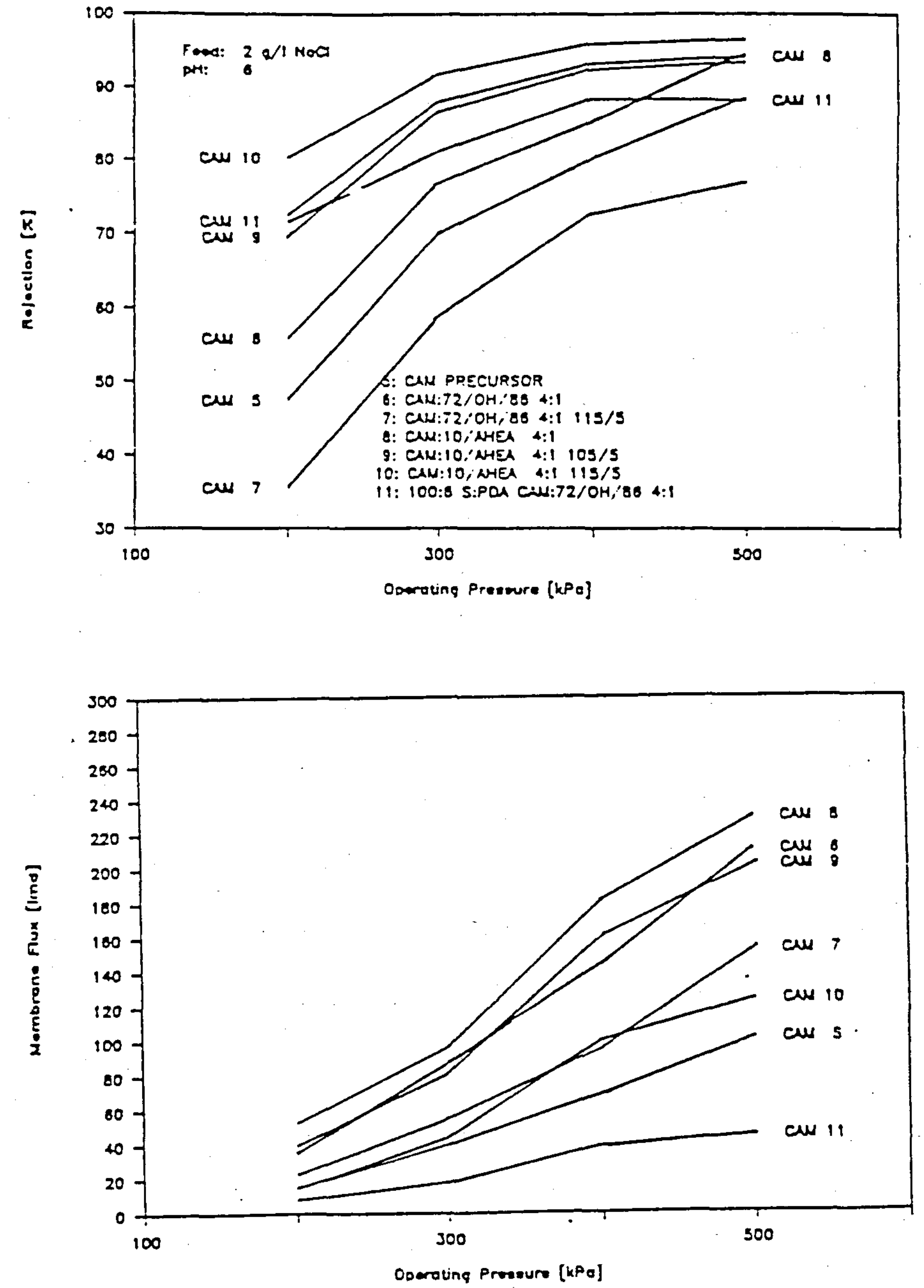


FIGURE 5:
The effect of operating pressure on the salt rejection and permeate flux of modified PVAM-C/SCI tubular membranes, filled with PVOH or AHEA-1

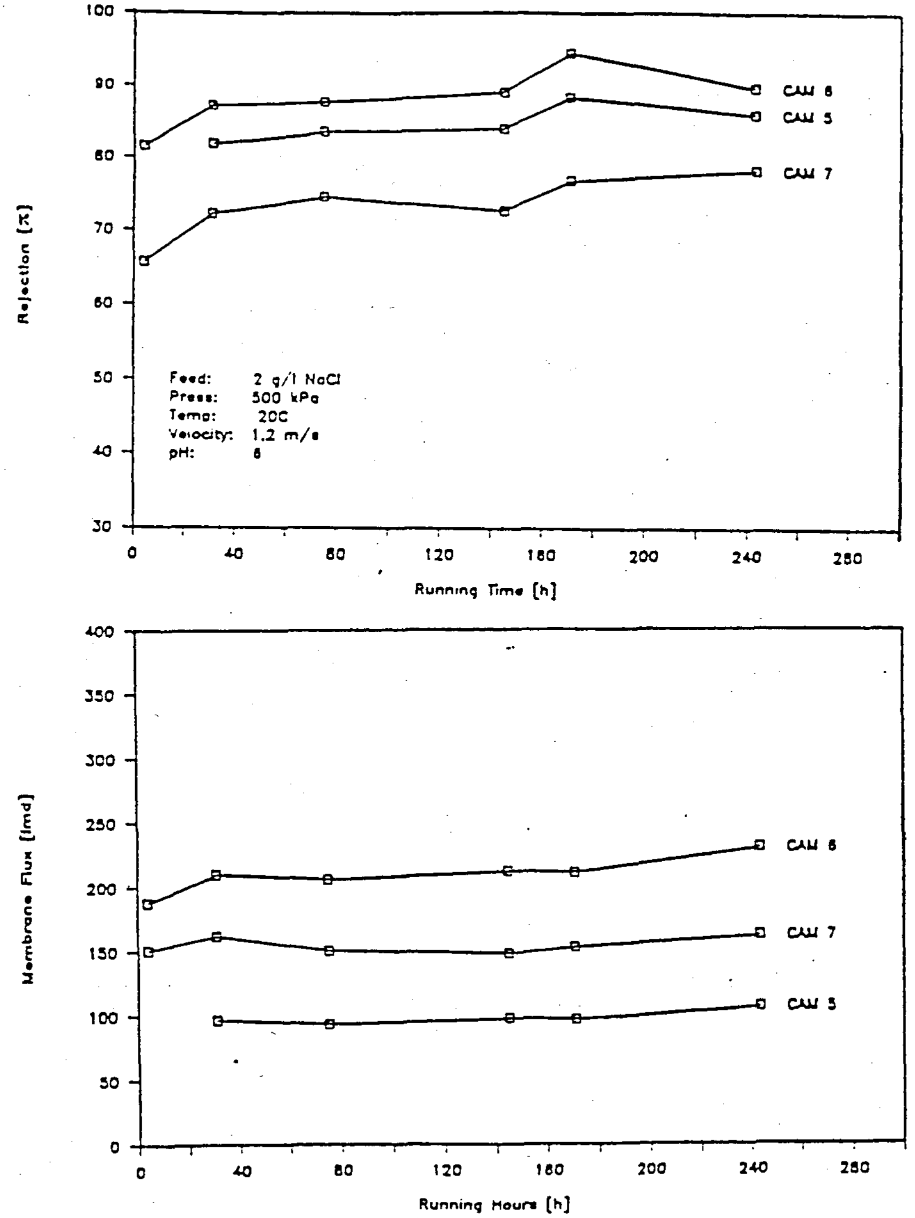


FIGURE 6:
Membrane performance stability of PVAM-C/SCl membranes containing PVOH, over an extended period

Incorporation of PVOH (0,25% mass of total precursor concentration) into the precursor solution again gave membranes which had significantly higher fluxes. In one case (CAM 6) such a membrane showed higher flux and rejection than the control PVI membrane. Early investigations into improving the RO performance of the basic PVAM/SCl membranes by modifying the composition of the PVAM precursor solution with PVOH were successful. The fluxes of PVAM/SCl membranes can be improved, without much decrease in their salt-retention properties, by the incorporation of the hydrophilic additive PVOH into the PVAM solution, e.g. membranes made from an admixture of PVAM + 20 m/m % PVOH (CAMOH 5 membranes) exhibited a performance of about 97% retention and 1100 lmd flux at standard operating conditions). This suggests that some of these membranes might perform satisfactorily at operating pressures below 2 000 kPa. Membranes prepared from a precursor solution of PVAM-C + PVOH (CAM 6) were tested and gave an RO performance of up to 90% retention and 200 lmd flux at a low operating pressure of 500 kPa, with a 2000 mg/l NaCl feed solution.

5.4 MEMBRANES MADE FROM HYDROXYL CONTANING POLYMERS, AND COPOLYMERS

Insolubilization of PVOH.

5.4.1 BACKGROUND

In recent years there has been a great deal of interest in poly(vinyl alcohol) (PVOH) UTF membranes. Being a material with good chemical stability, thermal stability, film-forming ability and high water permeability, PVOH has always seemed an attractive material for producing membranes. However, since it is highly hydrophilic, the unmodified PVOH membranes are highly permeable to both water and salts, so they need to be turned into completely insoluble materials with good mechanical properties. The most common ways of modifying PVOH are (i) copolymerization of vinyl acetate with hydrophobic (and hydrolitically-stable) monomers, followed by hydrolysis of acetate groups to produce vinyl alcohol copolymers, and (ii) the use of the hydroxyl groups of PVOH for crosslinking/modification reactions.

UTF composite membranes were to be created, from hydroxyl containing polymers (e.g. PVOH), on an asymmetic PES (PS) support.

Their application was to be primarily for brackish water desalination. Other applications could include organic rejections and protein rejections.

Membrane Requirements:

(1) Chlorine resistance;
(2) Hydrolytic stability over a reasonably wide pH range (3 - 11 or 4 - 10);
(3) Acceptable mechanical strength and thermal stability;
(4) Reasonable water flux at lowest possible operating pressure;
(5) Moderate to high salt-rejection capabilities (80 - 95%).

Although hydrolytic stability over a wide pH range is preferred, different membranes [which may be stable at near-neutral pH (say 6 to 8), pH 2 to 6 (acid stable) or pH 7 to 11 (base stable), for example] may be developed for different applications.

An operating pressure of 2 MPa will be used as "standard", but membranes should preferably also have good RO performances (particularly reasonable water fluxes) at pressures of 1 MPa and 0,5 MPa.

The three major areas of investigation were to include:

1. Commercial Poly(vinyl alcohol)

Commercial grades of PVOH as starting material were the obvious choices, since such membranes would be the most cost-effective. In this area of investigation, the emphasis was to be on suitable crosslinking reactions for the preparation of insoluble, stable membranes. The most obvious choices of reactions seemed to be esterification (e.g., with di-/triacid chlorides), etherification (e.g., with di-epoxides) and acetal formation (with di-aldehydes).

Variables which were studied included:

- Molecular mass of poly(vinyl alcohol)
- Concentration of PVOH
- Degree of hydrolysis of PVOH
- Type of crosslinking agent
- Concentration of X-linking agent
- Type of organic solvent (in interfacial X-linking reactions)
- Use of catalysts, and therefore catalyst concentration
- Soaking (dipping) time
- Draingage time
- Curing time and temperature
- Dry- or wet-storage time of membrane before testing
- Effect of post-treatment (various possibilities)

Crosslinking of PVOH with metal compounds was also to be investigated, although the few references to this in the literature focused mainly on the preparation of asymmetric membranes.

Apart from the aforementioned reactions (i.e., esterification, etherification, acetal formation and reaction with polyvalent metal ions) there appeared to be limited alternative routes. If crosslinking of PVOH is to be carried out by means of interfacial reactions, one serious limitation will be the choice of organic solvents for dissolving the respective crosslinking agents. Very few of the commonly used solvents for the crosslinking agents in question can be regarded as "safe" when PS/PES is used as the support material. Chlorinated solvents, in particular methylene chloride, ethers and ketones are commonly used in interfacial reactions. None of these can be used with PS (or PES).

2. Special PVOH activation (by introduction of specific pendant functionalities)

3. PVOH-containing copolymers, previously used for dynamic membranes

   (Polymers used for making dynamic membranes were used in a different way in order to make thin-film composite membranes which would operate at very low pressure with reasonable fluxes - see section 5.5.)

5.4.2 RESULTS AND DISCUSSION

The extensive experimental details pertaining to this section are described in an in-house report **[11]**. The following heat-activated chemical reactions of PVOH in solution-applied coatings were investigated.

5.4.2.1 Crosslinking of PVOH with metal-ions

To date, no salt-retention barriers were successfully formed when PVOH solutions were reacted with metal-ion-containing solutions of $CuCl_2$, 2 H_2O or $CuSO_4$, 5 H_2O. (No crosslinking took place.)

5.4.2.2 Crosslinking of PVOH with dialdehydes

No successful results were obtained from the heat treatment of aqueous solutions of PVOH and glutaraldehyde at 120°C. Results obtained by Cadotte **[12]** with formaldehyde-crosslinked PVOH membranes were also discouraging.

5.4.2.3 Crosslinking with di- and tetracarboxylic acids

The use of oxylic acid, succinic acid, citric acid and 1,2,3,4-butanetetracarboxylic acid as prospective crosslinking agents for PVOH (by ester-bond formation between -OH and -COOH groups) was unsuccessful. It appeared that no crosslinking had taken place.

Prompted by a recent publication of Jian and Ming **[13]**, in which dicarboxylic acids were used to crosslink PVOH in the presence of an acid catalyst to give membranes with a measure of salt-rejection, albeit with very low fluxes, the effect of sulphuric acid on the crosslinking of PVOH with oxalic acid was investigated. A PES support membrane was coated with a solution comprising: 20% PVOH, 1% oxalic acid and 0,5% H_2SO_4, then heat treated at 120°C/30 min. The RO performances of these membranes are shown in Table 21.

TABLE 21:

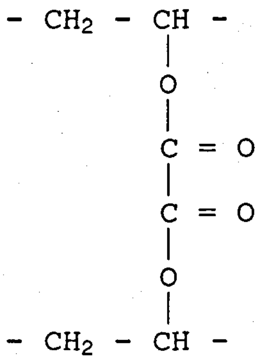
Reverse osmosis properties* of PVOH/oxalic acid membranes heat-cured in the presence of sulphuric acid**

Membrane	PVOH/OA1	PVOH/OA2	PVOH/OA3	PVOH/OA4	PVOH/OA5	PVOH/OA6
Rej %	68,2	65,2	71,0	65,1	74,6	75,1
Flux (lmd)	219	194	184	232	192	194

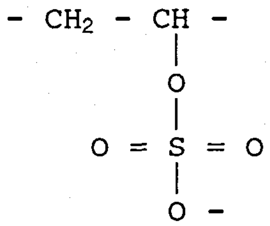
* Membranes tested at 25°C and 2 MPa on 2000 mg/ℓ NaCl feed

** Membrane coating solution; 2% PVOH (MM 125 000; 86-89% hydrolyzed), 1% OA, 0,5% H_2SO_4. Fabrication conditions: Wetting time 5 min, draining time 5 min, cured 30 min at 120°C.

Infra-red studies had shown that new absorption bands appeared at 1750 cm^{-1} and 1200 cm^{-1} **[13]**. It was suggested that structures such as



and



are formed during the crosslinking reaction, and that sulphuric acid was not only a catalyst, but also a reactant. During later studies on PVOH membranes, it was found that PVOH could be insolubilized in the presence of sulphuric acid as the only reactant (Section 5.4.2.6). It was not possible at this stage to predict if the crosslinking which occurred in the case of PVOH/oxalic acid/H_2SO_4 membranes involved formation of ester linkages or if the insolubilization or crosslinking reaction was caused solely by the sulphuric acid.

5.4.2.4 Membranes prepared from PVOH and poly(styrene sodium sulphonate) (PSSA-Na) blends

The preparation of interpolymer anionic composite reverse osmosis membranes was reported by Koyama et al. **[14]**. Membranes were prepared from PVOH as a membrane matrix and poly(styrene sulphonic acid) (PSSA) as a polyelectrolyte. These membranes performed reasonably well in reverse osmosis tests at high pressures of 8 MPa. Membranes heat treated at 120°C for 2 hrs exhibited water fluxes of 218-680 lmd and NaCl rejections of 88 - 93,4% (tested with 5000 ppm NaCl). PVOH/PSSA blend membranes were prepared in accordance with the method of Koyama **[14]**, (except that we used a PES support and the sodium salt of PSSA-PSS Na, they used a polypropylene support). Various casting-solutions and fabrication conditions were used. RO performances of these membranes were very poor; salt rejections were no higher than 5% and fluxes were extremely high, indicating that no (or minimal) crosslinking had taken place.

5.4.2.5 Reaction of PVOH with difunctional sulphuric acid compounds

Attempts were made to crosslink PVOH by formation of sulphonate (ester) linkages, using 4,5-dihydroxy-1,3-benzenedisulphonic acid Na salt (TIRON) as crosslinking agent and H_2SO_4 as catalyst.

Membranes were prepared by depositing various coating solutions on PES support membranes and heat curing them at different temperatures. RO performances of resulting membranes varied widely depending on the coating solution composition used.

Results obtained with flat-sheet membranes were rather inconsistent, making it difficult to reach any definite conclusions. It was nevertheless possible to see some general trends. The most significant observation was that no crosslinking reaction took place in the absence of sulphuric acid as catalyst. These membranes exhibited no NaCl rejection and extremely high water fluxes, regardless of the fact that they were heat-treated at 120°C for 20 minutes. The highest salt-rejections were obtained when only sulphuric acid, and no TIRON, was present in the coating solution.

<u>TABLE 22</u>:

Reverse osmosis properties* of PVOH membranes** prepared from difunctional sulphuric acid compounds (Solution 6) (2% PVOH; 0,1% H_2SO_4; O TRITON; 97,9% H_2O)

Membrane No.	6A	6B	6C	6D
Rejection (%)	88,4	82,4	89,3	86,7
Flux (lmd)	205	120	130	162

* Membranes tested at 2 MPa and 25°C on a 2000 mg/ℓ NaCl feed solution;

** Preparation conditions: wetting time 5 min; draining time 9 min; curing temperature 120°C; curing time 20 min.

No analytical studies (e.g., infra-red) were carried out in order to find out more about the structure of the crosslinked membranes. Consequently, there was no evidence to prove that the sulphonic acid compounds did in fact take part in the reaction. Since the reaction of PVOH with disulphonic acid compounds in the presence of H_2SO_4 is similar to that with dicarboxylic acids in the presence of H_2SO_4, the possibility that sulphuric acid alone was responsible for the crosslinking or insolubilization of PVOH must be considered in both cases.

5.4.2.6 Insolubilization of PVOH by heat-treatment in the presence of sulphuric acid

The reverse osmosis properties of membranes described above (Table 22) were sufficiently promising to warrant further investigation. A large number of PVOH/H_2SO_4 membranes were therefore prepared in an attempt to optimize their RO performance. The variables studied were: PVOH concentration, PVOH molecular mass, H_2SO_4 concentration, wetting time, draining time, curing time and curing temperature. Most of these studies were carried out using <u>flat-sheet</u> PES support membranes. Some of the results obtained are shown in Tables 23 to 31. (Different flat-sheet PES support membranes were used in the study, and unfortunately the type of support used for each individual experiment has not been recorded. It was clear that the type of support that was used also influenced the results, since the RO properties, especially water flux, sometimes varied considerably in spite of the fact that the same formulations and fabrication conditions were employed.)

TABLE 23:

The effect of PVOH[1] concentration on reverse osmosis properties[2] of PVOH/H_2SO_4 membranes

Membrane No.	1	2	3	4	5	6
PVOH conc.	0.5%	0.5%	1,0%	1.0%	2.0%	2.0%
H_2SO_4 conc.	0,2%	0.2%	0,2%	0,2%	0,2%	0,2%
Wetting time	5 min	5 min	5 min	5 min	5 min	5 min
Draining time	5 min	5 min	5 min	5 min	5 min	5 min
Curing time	20 min	20 min	20 min	20 min	20 min	20 min
Curing temp.	120°C	120°C	120°C	120°C	120°C	120°C
Rejection (%)	49,4	46,6	56,4	59,2	63,4	61,8
Flux (lmd)	1621	1598	1566	1519	1025	1185

1. PVOH MM 72 000 (SAARCHEM);
2. Membranes tested at 25°C and 2 MPa on a 2000 mg/ℓ NaCl feed.

It can be seen in Table 23 that an increase in the PVOH concentration resulted in an increase in NaCl rejection and a decrease in water flux.

TABLE 24:

The effect of H_2SO_4 concentration on the reverse osmosis performances[1] of PVOH/H_2SO_4 membranes

Membrane No.	1	2	3	4	5	6
PVOH[2] conc.	2%	2%	2%	2%	2%	2%
H_2SO_4 conc.	0,1%	0,1%	0,2%	0,2%	0,5%	0,5%
Wetting time	5 min	5 min	5 min	5 min	5 min	5 min
Draining time	5 min	5 min	5 min	5 min	5 min	5 min
Curing time	20 min	20 min	20 min	20 min	20 min	20 min
Curing temp.	125°C	125°C	125°C	125°C	125°C	125°C
Rejection (%)	57,0	54.1	60,0	65,8	77.1	81,6
Flux (lmd)	1448	1564	1017	978	817	761

1. Membranes tested at 25°C and 2 MPa on a 2000 mg/ℓ NaCl feed solution;
2. PVOH: MM 72 000 (SAARCHEM).

An increase in the sulphuric acid content of the coating solution resulted in an increase in salt rejection and a decrease in water flux. This is to be expected, since the sulphuric acid acts as a dehydration catalyst. A higher sulphuric acid content will therefore result in a higher degree of dehydration.

Table 25 shows that the molecular mass of the PVOH affects the reverse osmosis properties of the resulting membranes. Higher molecular mass PVOH membranes exhibited higher salt rejections and lower water fluxes than low molecular mass PVOH membranes.

TABLE 25:

The effect of PVOH molecular mass (MM) on reverse osmosis properties[1] of PVOH/H_2SO_4 membranes

	MM 72 000			MM 15 000		
Membrane No.	1	2	3	4	5	6
PVOH[2] conc.	2%	2%	2%	2%	2%	2%
H_2SO_4 conc.	0,1%	0,1%	0,1%	0,1%	0,1%	0,1%
Wetting time	5 min	5 min	5 min	5 min	5 min	5 min
Draining time	5 min	5 min	5 min	5 min	5 min	5 min
Curing time	20 min	20 min	20 min	20 min	20 min	20 min
Curing temp.	125°C	125°C	125°C	125°C	125°C	125°C
Rejection (%)	57,0	54,1	42,2	26.2	38,8	19,7
Flux (lmd)	1448	1564	2016	2780	2092	2967

1. Membranes tested at 25°C and 2 MPa on a 2000 mg/ℓ NaCl feed;
2. PVOH: Partially hydrolyzed grades; MM 72 000 (SAARCHEM); MM 15 000 (FLUKA).

Table 26 shows that an increase in the curing time increased the salt rejection and decreased the water flux. When the curing time was increased from 10 minutes to 30 minutes (at 125°C), the water flux was reduced drastically.

TABLE 26:

Effect of curing time on reverse osmosis properties[1] of PVOH/H_2SO_4 membranes

Membrane No.	1	2	3	4	5	6
PVOH[2] conc.	2%	2%	2%	2%	2%	2%
H_2SO_4 conc.	0,5%	0,5%	0,5%	0,5%	0,5%	0.5%
Wetting time	5 min	5 min	5 min	5 min	5 min	5 min
Draining time	5 min	5 min	5 min	5 min	5 min	5 min
Curing time	10 min	10 min	20 min	20 min	30 min	30 min
Curing temp.	125°C	125°C	125°C	125°C	125°C	125°C
Rejection (%)	53.4	47.2	77.1	81,6	80,1	83,7
Flux (lmd)	1266	1587	817	761	365	254

1. Membranes tested at 25°C and 2 MPa on a 2000 mg/ℓ NaCl feed;
2. PVOH MM 72 000 (SAARCHEM).

Table 27 shows that membranes which were heat-treated at 125°C exhibited higher salt rejections and lower water fluxes than those heat-treated at 100°C. It was difficult to maintain the temperature of the oven at a constant value. The moment the oven door was opened, the reading of the thermometer dropped immediately. The temperature values given therefore in the respective tables are the temperatures at which curing was supposed to take place, but in reality the temperatures were lower during the initial stage of the curing period. This practical problem was considered to be one reason why it was sometimes difficult to obtain reproducible results with PVOH/H_2SO_4 membranes.

TABLE 27:
The effect of curing temperature on reverse osmosis properties[1] of PVOH/H_2SO_4 membranes

Curing temp. (°C)	100			125		
Membrane No.	1	2	3	4	5	6
PVOH conc.	2%	2%	2%	2%	2%	2%
H_2SO_4 conc.	0,5%	0,5%	0,5%	0,5%	0,5%	0,5%
Wetting time	5 min	5 min	5 min	5 min	5 min	5 min
Draining time	5 min	5 min	5 min	5 min	5 min	5 min
Curing time	20 min	20 min	20 min	20 min	20 min	20 min
Rejection (%)	64,5	59,1	63,8	77,1	81,6	74,1
Flux (lmd)	968	1226	1164	817	761	820

1. Membranes tested at 25°C and 2 MPa on a 2000 mg/ℓ NaCl feed;
2. PVOH MM 72 000 (SAARCHEM).

The effect of operating pressure on the abovementioned membranes was also investigated.

TABLE 28:
The effect of operating pressure on the reverse osmosis properties[1] of PVOH/H_2SO_4 membranes

Membrane No.	1	2	3	4
PVOH[2]	2%	2%	2%	2%
H_2SO_4 concentration	0,1%	0,1%	0,1%	0,1%
Wetting time	5 min	5 min	5 min	5 min
Draining time	5 min	5 min	5 min	5 min
Curint time	20 min	20 min	20 min	20 min
Curing temperature	125°C	125°C	125°C	125°C
Rejection, 2 MPa	57,2%	43,7%	42,2%	49,0%
Flux (lmd), 2 MPa	1770	1577	2016	1867
Rejection, 1 MPa	46,6%	39,2%	38,4%	42,4%
Flux (lmd), 1 MPa	777	599	742	789
Rejection, 0,5 MPa[3]	38,4%	34,5%	35,3%	41,0%
Flux (lmd), 0,5 MPa[3]	455	334	366	211

1. Membranes tested at 25°C, 2000 mg/ℓ NaCl feed solution;
2. PVOH: MM 72 000 (SAARCHEM);
3. Pressure very unstable at 0,5 MPa. Results are probably not reliable.

The effect of various pretreatments on membrane performance was also investigated. Some membranes were subjected to immersion in a chlorine solution, some were dry-stored at room temperature for a few days, and some were stored in distilled water for 24 hours before being tested. The RO performances of these membranes are shown in Table 29.

TABLE 29:

Reverse osmosis properties[1] of PVOH/H_2SO_4 membranes[2] after various pretreatments

Membrane No.	1[3]	2[3]	3[4]	4[4]
Rejection Flux (lmd) at 2 MPa	68,7% 1655	63.7% 1688	70,5% 768	83,6% 827
Rejection Flux (lmd) at 1 MPa	60.9% 817	56,6% 916	67,5% 323	74,9% 373
Rejection Flux (lmd) at 0,5 MPa	49,8% 483	44,9% 543	67,2% 180	71,8% 215
Rejection (after 70 h) Flux at 2 MPa (after 70 h)	68,0% 1742	62,7% 1848	81,6% 761	82,9% 924

1. Feed solution: 2000 mg/ℓ NaCl;
2. PVOH (MM 72 000): 2%; H_2SO_4: 0.5%; membranes wetted for 5 min, drained for 5 min, and heat-treated for 20 min at 125°C;
3. Membranes 1 and 2 pretreated with chlorine before evaluation of RO performance;
4. Membranes 3 and 4 not treated with chlorine before evaluation of RO performance. Membrane 3 was dry-stored for a few days at room temperature; Membrane 4 was stored in distilled water for 24 hours before being tested.

Table 29 shows that after an operating time of 70 hours the NaCl rejection capability of Membranes 1 and 2 (pretreated with chlorine) remained unchanged, while the water flux increased markedly. This table also shows that the dry-stored membrane (no. 3) initially exhibited lower NaCl rejection, as well as lower water flux, than the wet-stored membrane (no. 4). After an operating time of 70 hours, the salt-rejection capability of the dry-stored membrane increased, while the flux remained the same. In the case of the wet-stored membrane (after 70 hours), the salt-rejection capability remained unchanged, but the water flux increased markedly. Membranes 3 and 4 exhibited similar NaCl rejections after 70 hours of testing, but the fluxes through Membrane 4 was considerably higher than that through Membrane 3. It is also clear that the flux of membranes which were pretreated with chlorine were double that of the membranes which were not subjected to chlorine pretreatment.

The membranes referred to in Table 29 were also tested at 2 MPa on a 500 mg/ℓ $MgSO_4$ feed solution. The results of this test are shown in Table 30.

TABLE 30:
$MgSO_4$ rejection of PVOH/H_2SO_4 membranes at 2 MPa
(first set)

Membrane No.	1	2	3	4
Rejection[1] Flux[1] (lmd)	83,0% 1375	78.4% 1548	90,1% 541	91,3% 620
Rejection[2] Flux[2] (lmd)	83,3% 1330	78,6% 1498	91,2% 525	91,7% 600

1. After an operating time of 2 hours;
2. After an operating time of 3,5 hours.

$MgSO_4$ rejections of 80 - 90% were obtained, but even after a relatively short period of testing it was clear that the fluxes were decreasing with time.

The $MgSO_4$ rejection of another set of PVOH/H_2SO_4 membranes was also evaluated, and the results are given in Table 22.

TABLE 31:
$MgSO_4$ rejection[1] of PVOH/H_2SO_4 membranes[2]
(second set)

Membrane No.	1	2	3	4
Rejection[3] Flux[3] (lmd)	78,0% 1548	85,7% 984	82,7% 1300	87,0% 772
Rejection[4] Flux[4] (lmd)	78.5% 1485	85.8% 950	82,1% 1265	87,0% 746

1. Membranes tested at 2 MPa on a 500 mg/ℓ $MgSO_4$ feed solution;
2. PVOH (MM 72 000): 2%; H_2SO_4: 0,1%; membrane wetted for 5 min, drained for 5 min, and heat-treated for 20 min at 125°C;
3. After an operating time of 2 hours;
4. After an operating time of 3,5 hours.

The chlorine stability of the membranes shown in Table 31 was evaluated as a function of operating time. The membranes were tested at 25°C and 2 MPa on a 2000 mg/ℓ NaCl feed solution, and 100 ml chlorine (NaOCl) was added to 10 ℓ feed solution at certain times during the test period. The results of this test are shown in Figures 7 and 8.

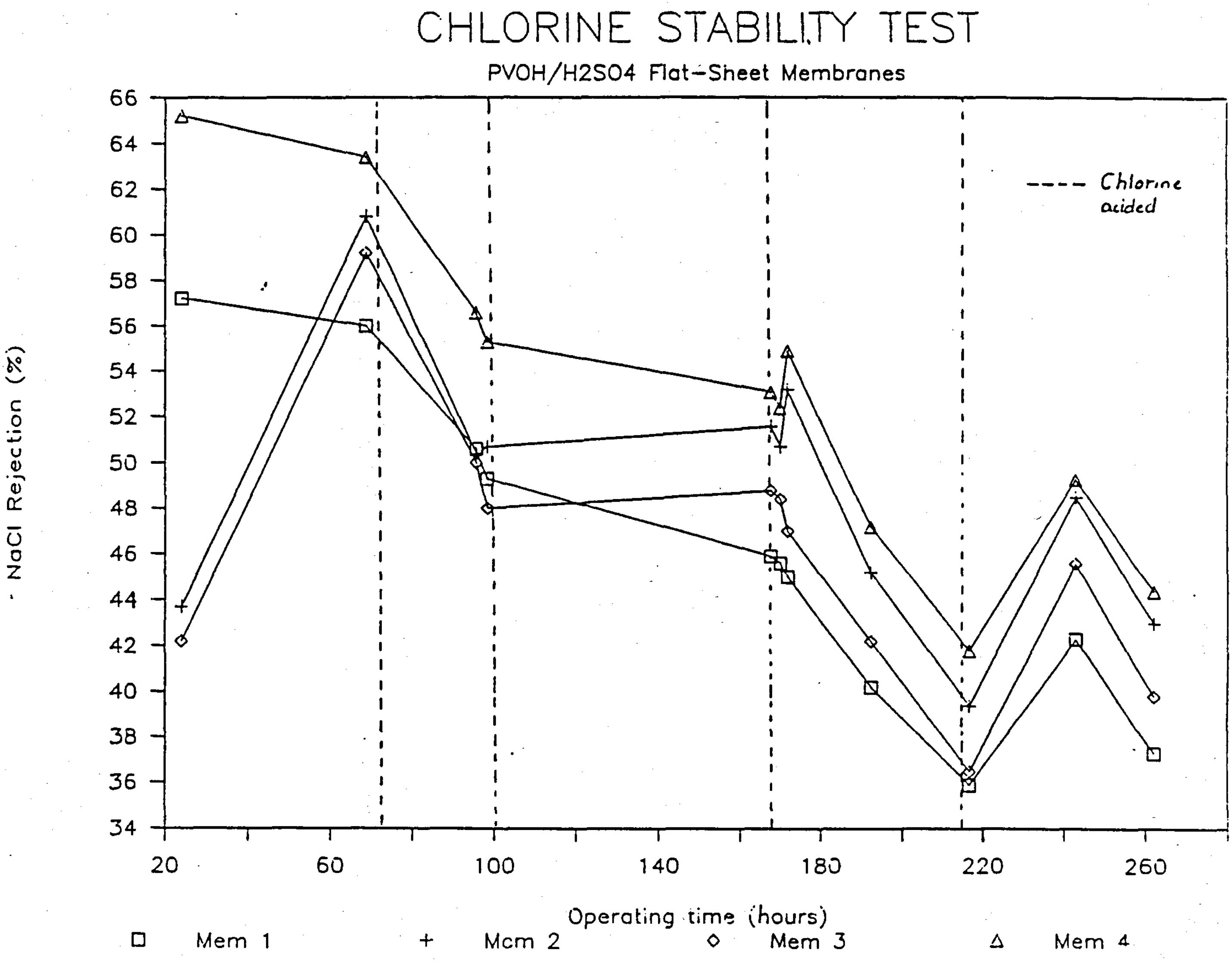


FIGURE 7:

Chlorine stability test: PVOH/H_2SO_4 flat-sheet membranes.

Salt rejection (%) v/s operating time

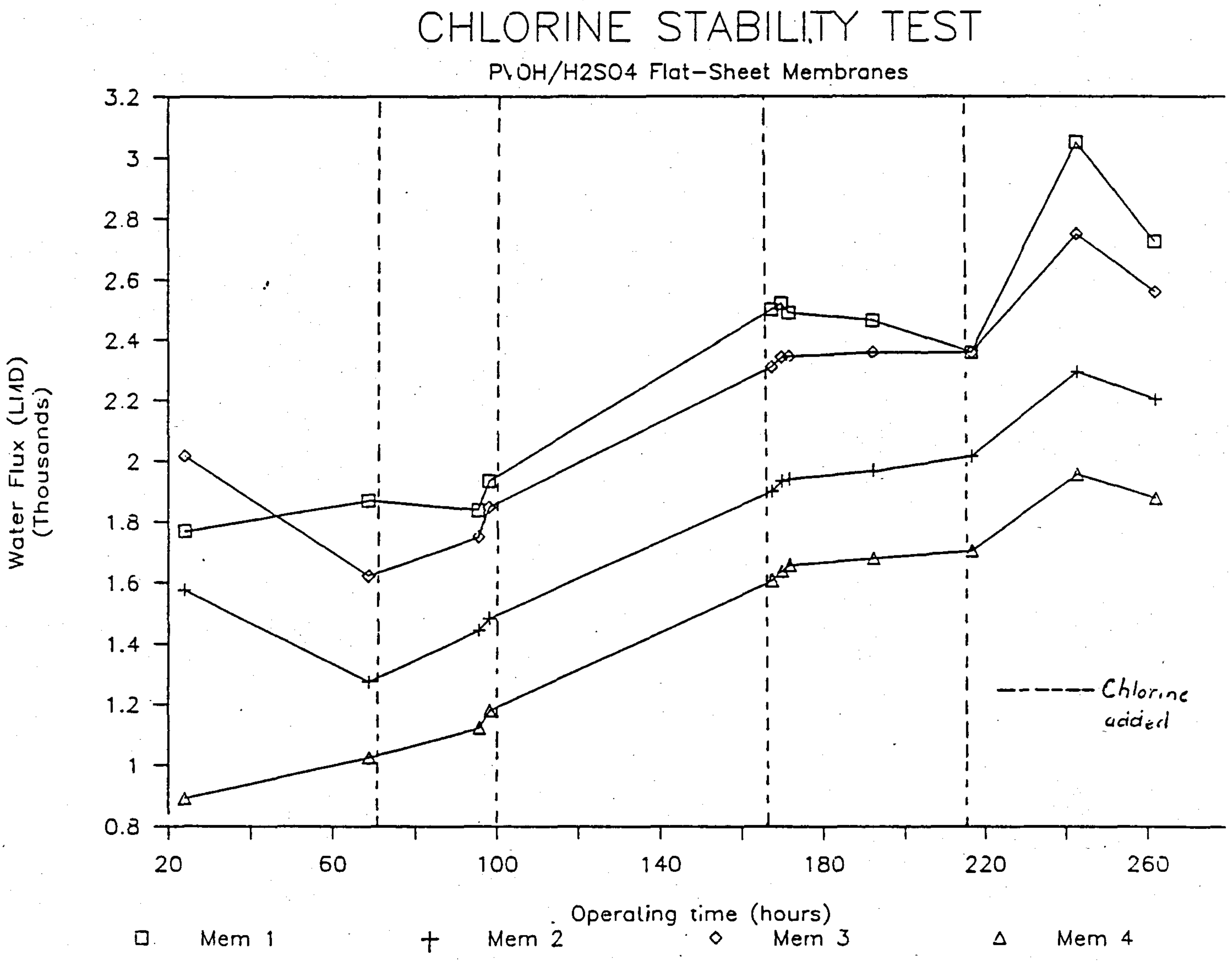


FIGURE 8:
Chlorine stability test: PVOH/H_2SO_4 flat-sheet membranes.
Water flux (%) v/s operating time

$PVOH/H_2SO_4$ coatings were also deposited on 13 mm tubular PES support membranes. The compositions of the coating solutions and the membrane fabrication conditions are summarized in Table 32.

<u>TABLE 32</u>:
Compositions of coating solutions and membrane fabrication conditions: Tubular $PVOH/H_2SO_4$ UTF membrnaes

Membrane	LP-1	LP-2	LP-3	LP-4	LP-5	LP-6	LP-7	LP-8
PVOH 72 000 (mass %)	1,0	2,0	1,0	2,0	1,0	2,0	1,0	2,0
Conc. H_2SO_4 (mass %)	0,4	0,4	0,8	0,8	0,4	0,4	0,8	0,8
Support predraining time (min)	5	5	5	5	5	5	5	5
Wetting time (min)	5	5	5	5	5	5	5	5
Draining time (min)	5	5	5	5	5	5	5	5
Curing time (min)	20	20	20	20	20	20	20	20
Curing temp. (°C)	110	110	110	110	130	130	130	130

The NaCl rejections and fluxes of tubular $PVOH/H_2SO_4$ UTF membranes (LP-1 to LP-8), monitored at different operating pressures before and after treatment of the membranes with chlorine, are summarized in Table 33.

TABLE 33:

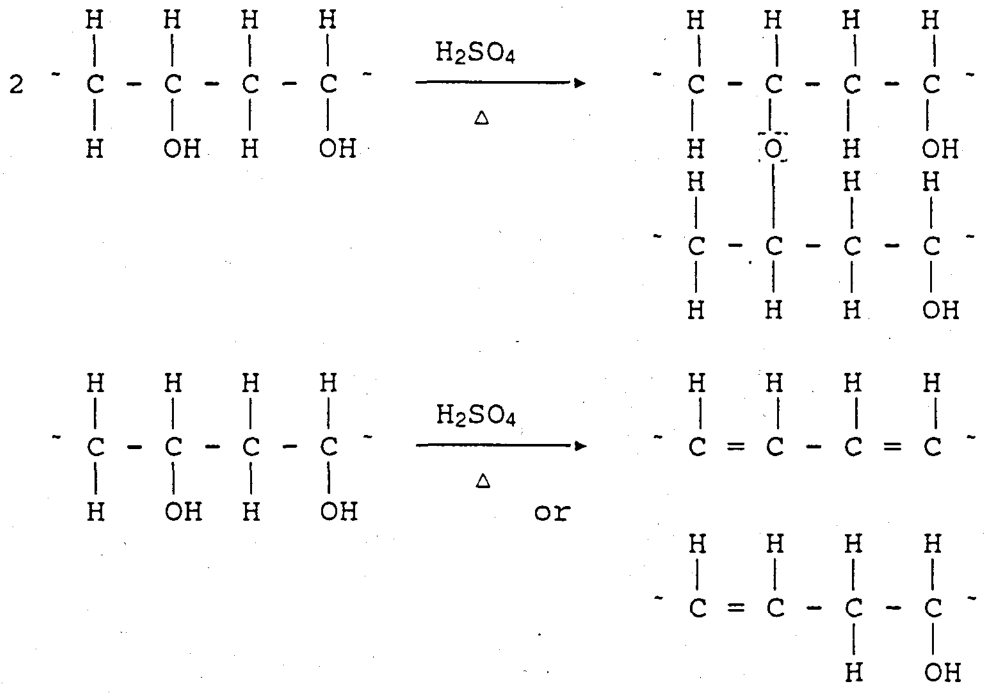
Flux and NaCl retention of tubular PVOH/H_2SO_4 UTF membranes at different operating pressures

Membrane		LP-1	LP-2	LP-3	LP-4	LP-5	LP-6	LP-7	LP-8
Before chlorine treatment Run. Time (hours)									
65	Flux (lmd) at 2 MPa	410	537	291	285	365	293	360	339
	Retention (%)	57,7	58,4	56,4	64,3	54,3	65,9	50,9	56,4
69	Flux (lmd) at 1,5 MPa	293	377	199	194	250	163	291	230
	Retention (%)	49,5	49,1	46,8	55,2	50,0	56,0	41,6	47,9
71	Flux (lmd) at 0,5 MPa	79	107	55	53	69	50	70	63
	Retention (%)	24,1	24.8	19,5	27,5	22,0	28,2	18,9	23,0
After first chlorine treatment									
81	Flux (lmd) at 2 MPa	438	606	300	306	428	373	357	348
	Retention (%)	61,2	61,1	61,7	68,6	62,5	67,6	59,0	62,5
146	Flux (lmd) at 1,5 MPa	410	543	293	303	421	386	355	357
	Retention (%)	56,8	55.8	55.8	63,3	55,2	60,1	51,7	56,3
173	Flux (lmd) at 2 MPa	492	620	339	360	516	466	435	438
	Retention (%)	58,7	57,7	58,0	65.0	56,7	62,1	53,8	57,7
176	Flux (lmd) at 1,5 MPa	350	465	248	300	373	339	318	314
	Retention (%)	52.0	51,5	51,5	58,7	50,5	55,9	47,4	51,5
194	Flux (lmd) at 1 MPa	227	301	159	170	243	199	205	204
	Retention (%)	40,5	40.3	40,0	46,5	38,8	44,3	35,5	40,0
196	Flux (lmd) at 0,5 MPa	96	127	67	71	100	85	84	81
	Retention (%)	22,9	21,2	20,9	24,9	21,4	23,9	18,1	20,7
After second chlorine treatment									
241	Flux (lmd) at 0,5 MPa	110	75	79	84	123	114	106	106
	Retention (%)	24,0	24,0	23,3	27,3	22,7	24,9	22,5	22,7
313	Flux (lmd) at 0,5 MPa	120	160	91	95	145	134	130	130
	Retention (%)	22.4	22.1	20,8	24,7	19.7	22,6	19.7	20,8

Note: Membranes tested at 20°C and pH 6 on a 2 000 mg/ℓ NaCl feed solution.

Clearly, there were no significant differences between the RO properties of these membranes. The fluxes and salt rejections obtained at 2 MPa were promising. However, the fluxes obtained with tubular membranes were markedly lower than those obtained with flat-sheet membranes. At pressures below 1 MPa both the fluxes and the NaCl rejections were too low to be of practical use. Treatment of the membranes with chlorine resulted in an increase in flux, but apparently this treatment had no significant influence on salt rejection.

Following a study of the acid-catalyzed dehydration of PVOH, causing insolubilization, it became clear that the dehydration of PVOH by sulphuric acid can result in crosslinking through formation of ether linkages, double-bond formation through β-elimination, or a combination of both processes:



It is difficult to predict which process will predominate. However, during the preparation of PVOH/H_2SO_4 membranes, heat-treatment of the membranes resulted in colour development. As the H_2SO_4 concentration, curing temperature and curing time were increased, the colour of the membranes changed from a very light brown to almost black. This would indicate that double-bond formation definitely predominated. It is also known that once a double-bond is formed, the formation of the next double-bond occurs much easier. It is therefore assumed that dehydration of PVOH resulted in the formation of a polyacetylene structure (or at least that section of the PVOH molecules were converted to polyacetylene structures), and that the presence of conjugated unsaturation was responsible for colour development. On the other hand, the possibility that some ether crosslinks were formed cannot be excluded. Analytical studies, such as UV and FTIR, are required in order to clarify this matter.

5.4.2.7 Heat treatment of PVOH in presence of p-Toluenesulphonic acid (p-TSA)

Flat-sheet PES support membranes coated with aqueous solutions of PVOH (2%) and p-TSA (varying quantities of 0,5-1,5%) were heat-treated (100-130°C) for various periods of time. These PVOH-based membranes remained water soluble.

5.4.2.8 Heat treatment of blends of PVOH and maleic acid copolymers (MVE-co-MA)

Membranes were prepared from blends of PVOH and a copolymer of methyl vinyl ether/maleic anhydride (MVE-co-MA). These copolymers of methyl vinyl ether and maleic anhydride are marketed under the tradename GANTREZ AN by the GAF Coporation. ICI markets the copolymer as VISCOFRES. GAF offers the MVE-co-MA in several grades: AN-119, 139, 149 and 169.

The use of different ratios of PVOH: MVE-co-MA were evaluated during the study. Only flat-sheet membranes were prepared. The effect of fabrication conditions on membrane performance was investigated. Special attention was given to the effect of curing temperature, curing time and heat-treatment in the presence and absence of an acid catalyst (sulphuric acid). The compositions of coating solutions and membrane fabrication conditions of PVOH/MVE-co-MA membranes, which were heat-treated at different temperatures in the presence and absence of H_2SO_4 catalyst, are given in Table 34. The reverse osmosis properties of these membranes were tested at different pH values of the feeds solution. The results of this study are shown in Table 35, as well as in Figures 9 to 11.

<u>TABLE 34</u>:

Compositions of coating solutions and membrane fabrication conditions:
PVOH-MVE-co-MA membranes (Series 1)

Coating Solution	PVOH/MVE-co-MA 1	PVOH/MVE-co-MA 2	PVOH/MVE-co-MA 3
PVOH[1] (mass %)	1,0	1,0	1,0
MVE-co-MA[2] (mass %)	1,0	1,0	1,0
H_2SO_4 (mass %)	-	-	0,5
Support predraining time (min)	5	5	5
Wetting time (min)	10	10	10
Draining time (min)	8	8	8
Curing time (min)	20	20	20
Curing temperature (°C)	125	130 - 135	125

1. PVOH: MM 72 000 (SAARCHEM)
2. MVE-co-MA: GANTREZ AN-149

TABLE 35:

Reverse osmosis properties[1] of PVOH/MVE-co-MA blend membranes as a function of pH

Membrane	1			2			4		
pH	3	7	11	3	7	11	3	7	11
After 51.6 hours									
Rejection (%)		34,1			10,7			6,4	
Flux (lmd)		507			501			324	
After 100.3 hours									
Rejection (%)			65,1			53,8			71,6
Flux (lmd)			546			306			731
After 128.7 hours									
Rejection (%)	42,1			40,6			52,7		
Flux (lmd)	552			341			1076		
After 146.1 hours									
Rejection (%)		59.2			50,0			70,1	
Flux (lmd)		520			294			661	
After 151.1 hours									
Rejection (%)			67,8			61,0			75,1
Flux (lmd)			475			247			665
After 178.5 hours									
Rejection (%)	38,8			39,6			54,2		
Flux (lmd)	457			290			833		
After 218.2 hours									
Rejection (%)		64,3			60,9			76,1	
Flux (lmd)		423			214			537	
After 221.0 hours									
Rejection (%)			74,3			71,2			80,9
Flux (lmd)			396			180			563
After 223.7 hours									
Rejection (%)	38.4			46.0			50,3		
Flux (lmd)	396			226			757		

1. Membranes tested 20°C and 2 MPa on a 2000 mg/ℓ NaCl feed solution.

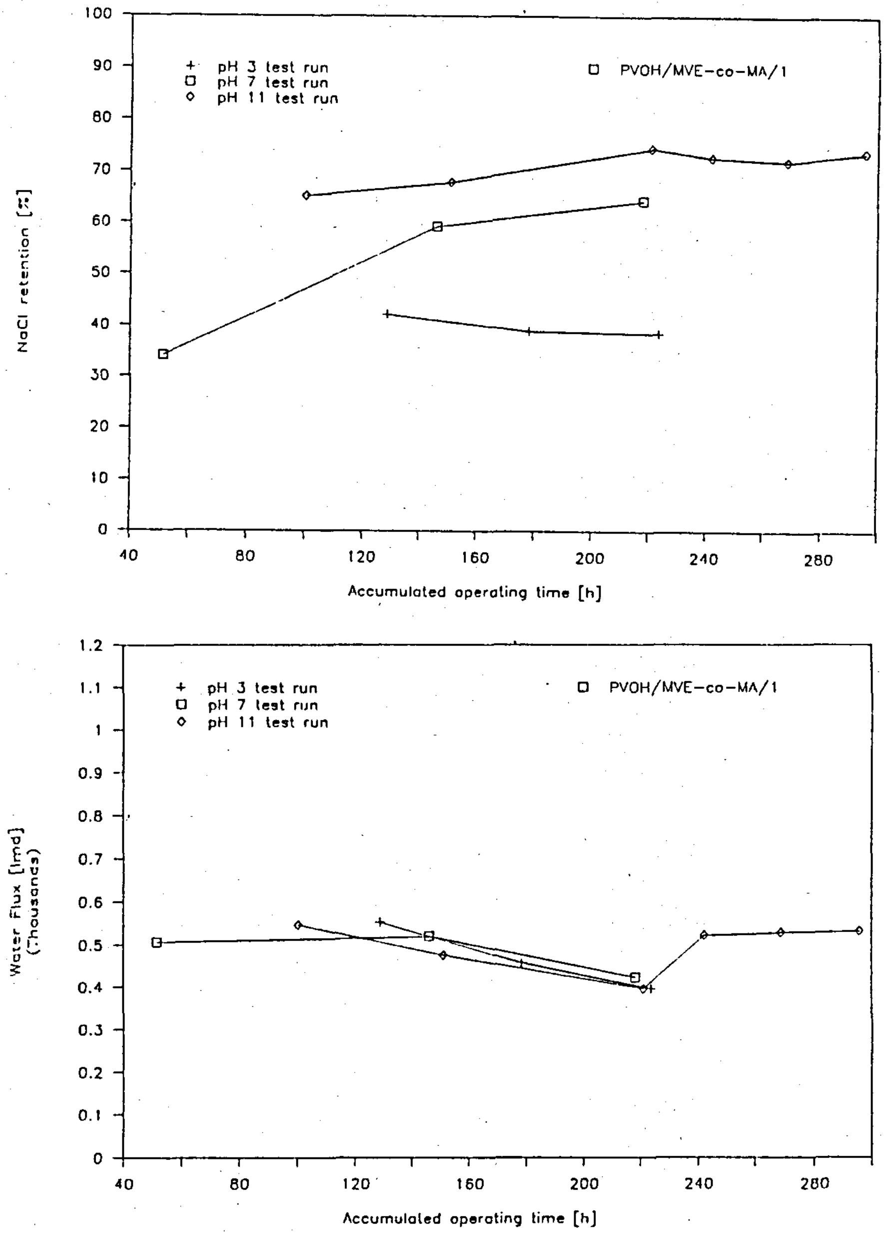


FIGURE 9:
NaCl retention and permeate flux of PVOH/MVE-co-MA/1 membranes at different pH values

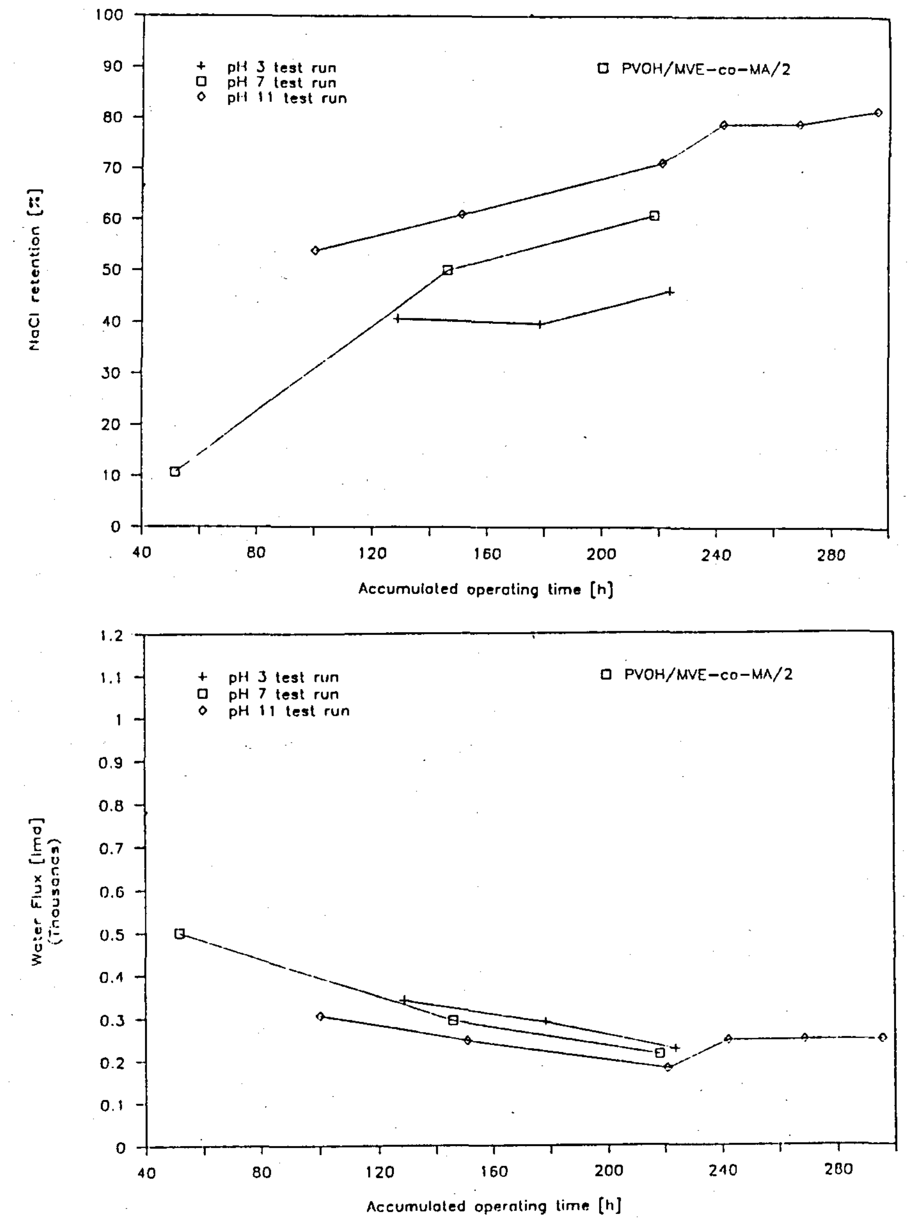


FIGURE 10:
NaCl retention and permeate flux of PVOH/MVE-co-MA/2 membranes at different pH values

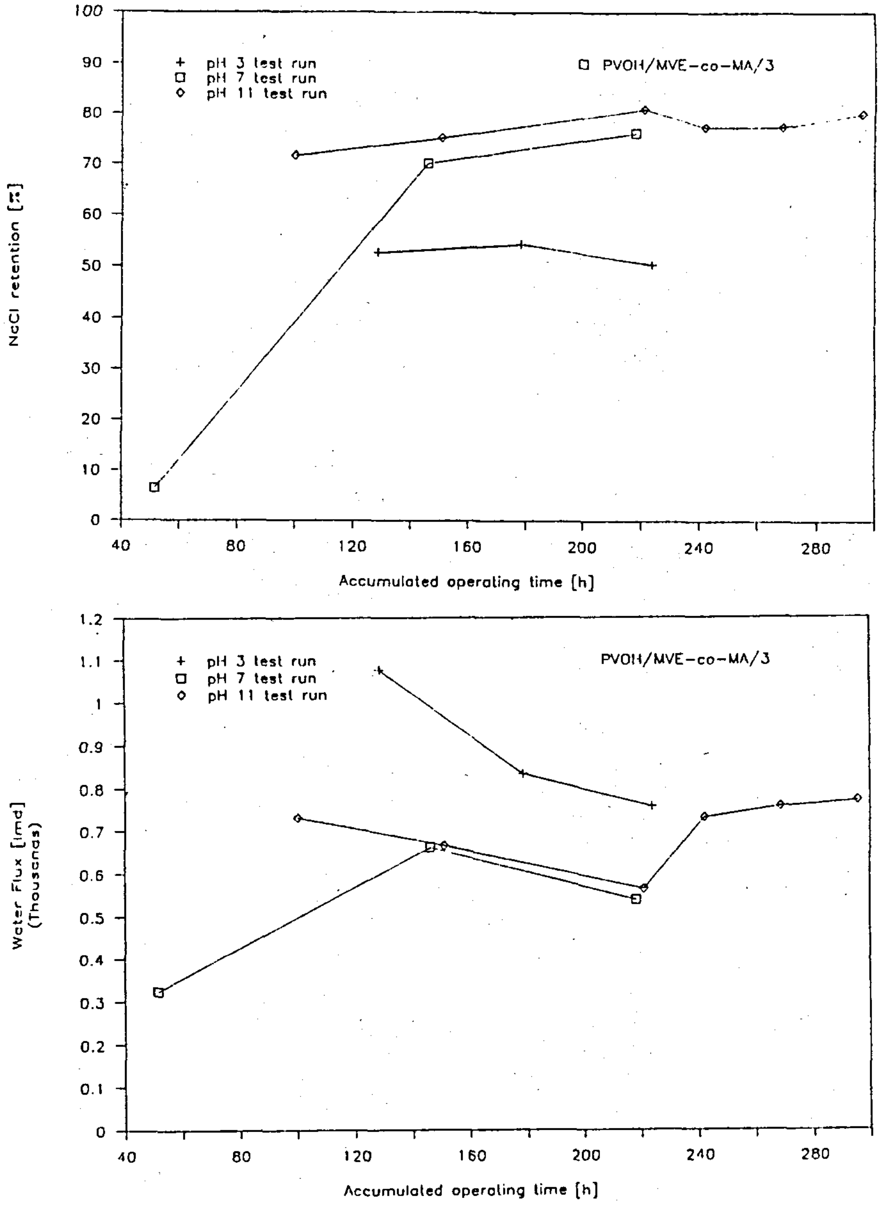


FIGURE 11:

NaCl retention and permeate flux of PVOH/MVE-co-MA/3 membranes at different pH values

The NaCl rejections of PVOH/MVE-co-MA membranes at pH 3, 7 and 11 have been shown in Figures 9 to 11. The highest salt rejections were obtained at pH 11, while the lowest rejections were measured at pH 3. The fluxes of these membranes at different pH values showed a complex behaviour. The best results were obtained with PVOH/MVE-co-MA membranes which were heat-treated in the presence of sulphuric acid (PVOH/MVE-co-MA/3). Membranes which were heat-treated at 130 - 135°C (PVOH/MVE-co-MA/2) exhibited higher NaCl rejections and lower fluxes than membranes which were heat-treated at 125°C (PVOH/MVE-co-MA/1).

The reverse osmosis performance of these PVOH/MVE-co-MA membranes (compositions are shown in Table 34) at pH 11, after an operating time of 295 hours, are shown in Table 36.

TABLE 36:

Reverse osmosis performance[1] of PVOH/MVE-co-MA blend membranes at pH 11

Membrane No.	1		2		3	
	Flux (lmd)	Rej. (%)	Flux (lmd)	Rej. (%)	Flux (lmd)	Rej. (%)
Operating time (h)						
100.3	546	65,1	306	53,8	731	71,6
151,1	475	67,8	247	61,0	665	71,5
221,0	396	74.3	180	71,2	563	80,9
242,1	521	72.6	247	78,9	731	77,3
268,7	528	71,9	248	78,9	757	77,4
295,7	531	73,6	249	81,6	771	78,0

1. Membranes tested at 20°C and 2 MPa on a 2000 mg/ℓ NaCl feed solution.

The flux and NaCl rejection of these membranes had apparently stabilized at pH 11 after an operating time of 295 hours. It is important to note that the membranes were continuously subjected to different pH cycles for 224 hours before they were allowed to equilibrate at pH 11 (during the last 72 hours of the test period). After an operating time of 295 hours, the salt rejections of Membranes 1 and 2 increased, while the water fluxes decreased. In the case of Membrane 3 (after 295 hours), both the salt rejection and the flux increased.

Heat treatment of blends of PVOH and MVE-co-MA results in ester formation between -OH groups of PVOH and the anhydride groups (or carboxylic acid groups, when hydrolyzed) of MVE-co-MA. Each of these two polymers act as a crosslinking agent for the other. The fact that all these polymer blend membranes exhibited some level of salt rejection, as well as relatively low water fluxes, indicated that crosslinking did occur in all cases. It is of course, obvious that these crosslinked PVOH/MVE-co-MA membranes will contain a considerable amount of free carboxyl groups, since each anhydride group yields two carboxylic acid groups upon hydrolysis in aqueous medium. The pH dependence of salt rejection and water flux can therefore be explained in terms of different degrees of ionization of the carboxyl groups in the membrane at different pH values.

When the RO properties of membranes which were heat-treated in the absence of H_2SO_4 are compared with those of membranes heat-treated in the presence of H_2SO_4, it is clear that the crosslinked structures of these two types of membranes were different. When these experiments were conducted, it was thought that the sulphuric acid will act only as an esterification catalyst. It this was true, membranes heat-treated in the presence of H_2SO_4 should have exhibited lower fluxes than membranes prepared in the absence of H_2SO_4. The results of this study indicate that the reaction in the presence of H_2SO_4 was more complex than originally expected. At this stage, it is not possible to give an explanation of the mechanism of crosslinking of these PVOH/MVE-co-MA blend membranes in the presence of H_2SO_4 catalyst. Analytical studies are necessary in order to obtain more information about the reaction and the structure of crosslinked membranes.

In multicomponent polymer systems, a microphase separation of the polymeric components is often observed at the molecular level. Such a phase separation is commonly observed in block and graft copolymers and in many polymer blends. Phase separation is temperature-dependent. Homogeneity is a prime criterion for membrane strength and selectivity and therefore coating solution compositions and membrane drying procedures should be selected in such a way that phase separation is minimized.

Gryte et al. **[15]** have shown that solutions of PVOH and MVE-co-MA in water are highly compatible and that this compatibility is temperature independent. Therefore, phase separation is not a problem in this particular two-component system. Since both PVOH and MVE-co-MA are hydrophilic and water soluble, crosslinking of the chains into a three-dimensional network is essential to maintain the integrity of the membrane in an aqueous environment. In the PVOH/MVE-co-MA system, the gel network is caused by the intermolecular esterification of the functional groups of PVOH and MVE-co-MA. The charge character of the crosslinked membranes results from the presence of carboxylate groups of the hydrolyzed but unesterified MVE-co-MA.

In these PVOH-MVE-co-MA membranes, electrolyte rejection occurs by an ion-exclusion mechanism, which is caused by the fixed charges of the carboxyl groups. Such is not the case if a neutral PVOH crosslinking agent such as dialdehyde is used. In this latter case, the PVOH domains would be non-ionic, and thus a non-permselective path would exist though which electrolyte could flow accross the membrane. Thus, the application of a polyfunctional polycarboxylic acid (hydrolyzed MVE-co-MA) in this work serves two purposes: to provide effective crosslinking and, at the same time, to impart a fixed charge character to the crosslinked PVOH matrix component.

After consulting the literature **[15-17]** it became clear that the ionization of the first and second carboxyl groups of maleic acid is rather complex and that it occurs at different pH values. The pH-dependence of the flux and salt rejection properties of PVOH/MVE-co-MA membranes must therefore be interpreted in terms of this complex ionization behaviour of the maleic acid residues in these polymer blend membranes.

5.4.2.9 Heat treatment of PVOH in the presence of $K_2S_2O_8$

It was mentioned in an Indian patent **[18]** that PVOH can be crosslinked with potassium persulphate to give a mechanically stable gel. This crosslinked, hydrophilic gel was apparently used as a packaging material. No other references to crosslinking of PVOH with $K_2S_2O_8$ could be traced during the period of study. Based on this one available abstract, it was decided to investigate the possibility of using this reaction in the preparation of crosslinked PVOH reverse osmosis membranes. The results discussed in this section refer only to the initial work on this particular type of membrane. (It should be noted that the reverse osmosis properties of PVOH/$K_2S_2O_8$ membranes were later studied extensively, by Deon Bezuidenhout, during the period January 1990 - May 1991, and will be reported on in the following final report.)

Membranes were initially prepared by depositing the PVOH/$K_2S_2O_8$ solutions on flat-sheet PES supports. The compositions of the coating solutions and membrane fabrication conditions are summarized in Table 37.

TABLE 37:
Compositions of coating solutions and membrane fabrication conditions:
PVOH/$K_2S_2O_8$ flat-sheet membranes

Solution	1	2	3	4
PVOH[1] (mass %)	2	3	-	-
PVOH[2] (mass %)	-	-	2	3
$K_2S_2O_8$ (mass %)	0,5	1,0	0,5	1,0
Support predraining time (min)	5	5	5	5
Wetting time (min)	10	10	10	10
Draining time (min)	5	5	5	5
Curing time (min)	20	20	20	20
Curing temperature (°C)	100	100	100	100

1. PVOH MM 72 000, partially hydrolyzed (SAARCHEM).
2. PVOH MM 115 000, fully hydrolyzed (ALDRICH).

The effect of heat-treatment time on the RO properties of PVOH/$K_2S_2O_8$ membranes was studied using membranes from Solution 1 (Table 37). In this experiment, the fabrication conditions were the same as those shown in Table 37, except that the membranes were cured at 85°C for different periods of time. Membranes were tested at 2 MPa, 20°C and pH 6,5 on a 1000 mg/ℓ $MgSO_4$ solution, as well as on a 2000 mg/ℓ NaCl feed solution. The results of this experiment are shown in Figures 12 to 15.

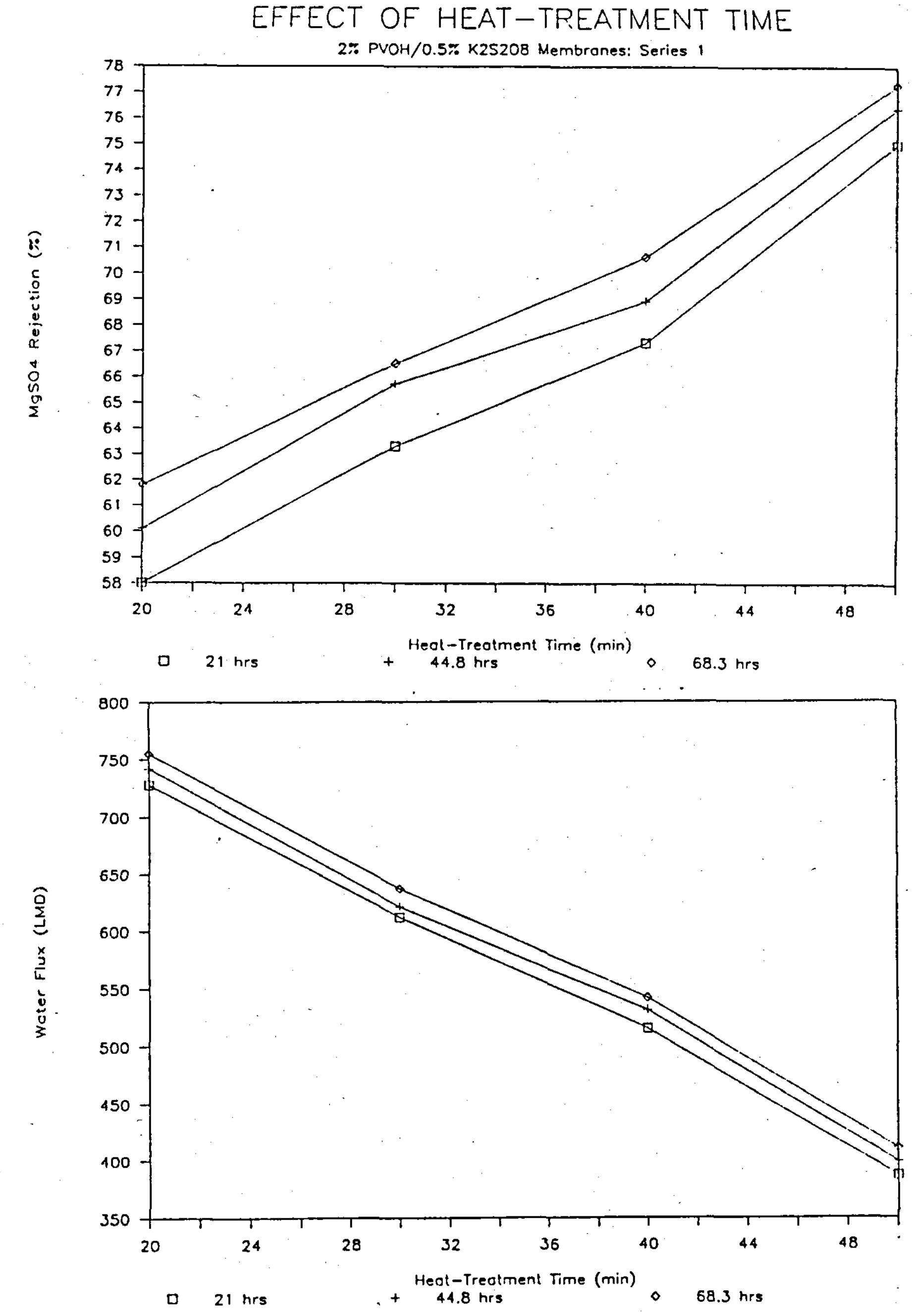


FIGURE 12:

Effect of heat treatment on the performance of PVOH/K_2SO_4 membranes.
(Series 1) (2% PVOH; 0,5%; $K_2S_2O_8$)

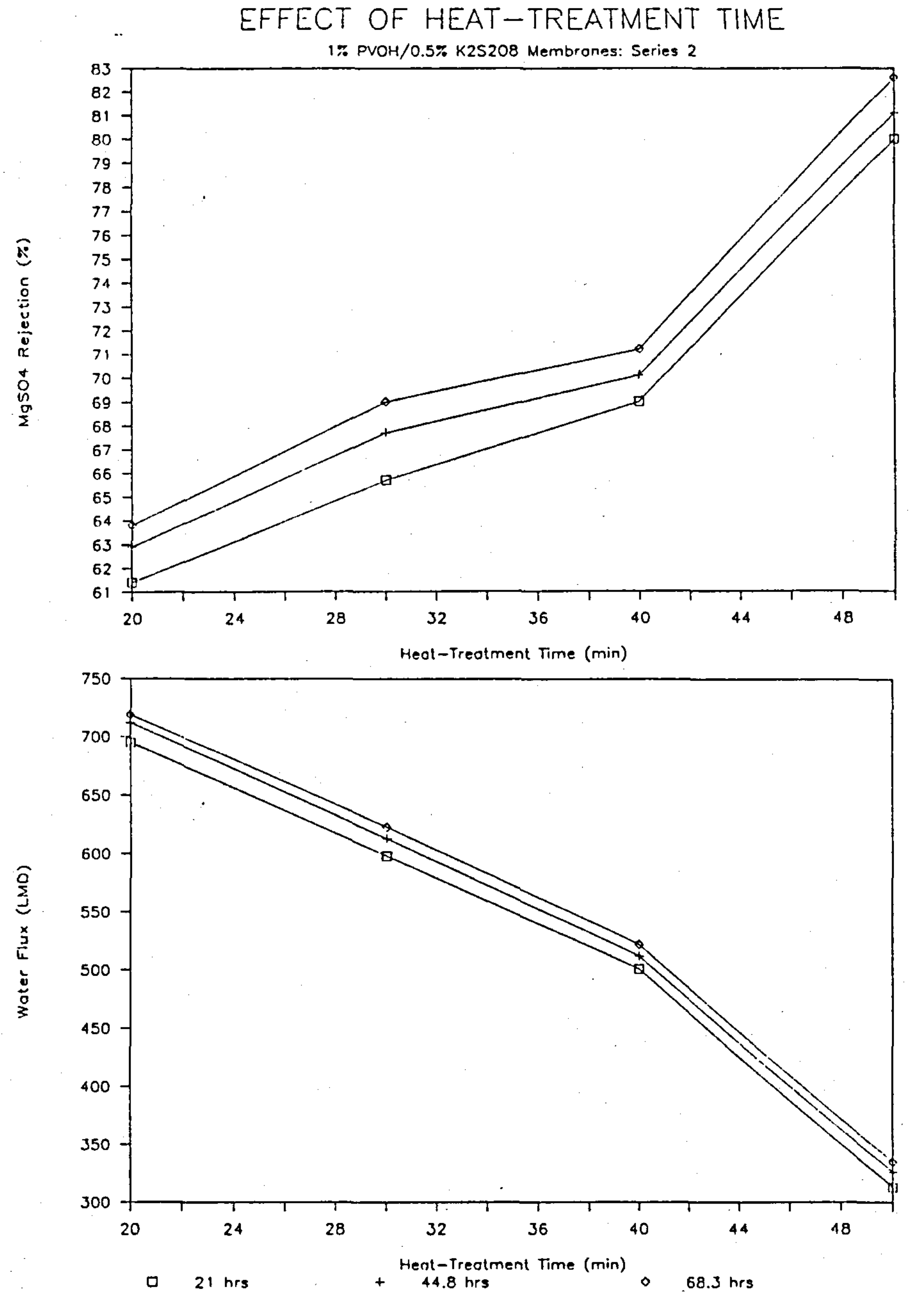


FIGURE 13:

Effect of heat treatment on the performance of PVOH/$K_2S_2O_8$ membranes.
(Series 2) (1% PVOH; 0,5%; $K_2S_2O_8$)

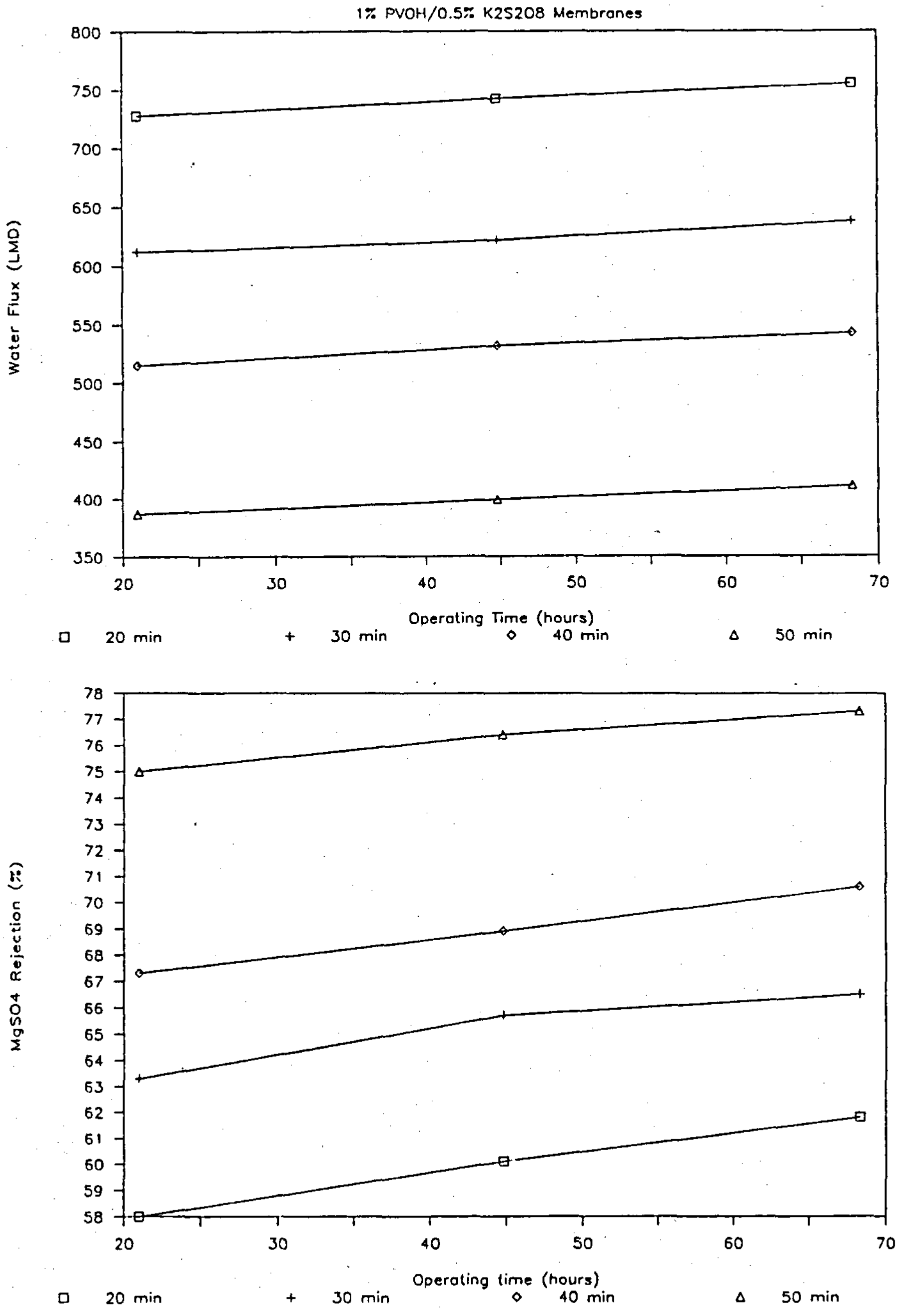


FIGURE 14:

Effect of operating time on the RO performance of PVOH/$K_2S_2O_8$ membranes, treated for various periods of time. (Series 2) (1% PVOH; 0,5%; $K_2S_2O_8$)

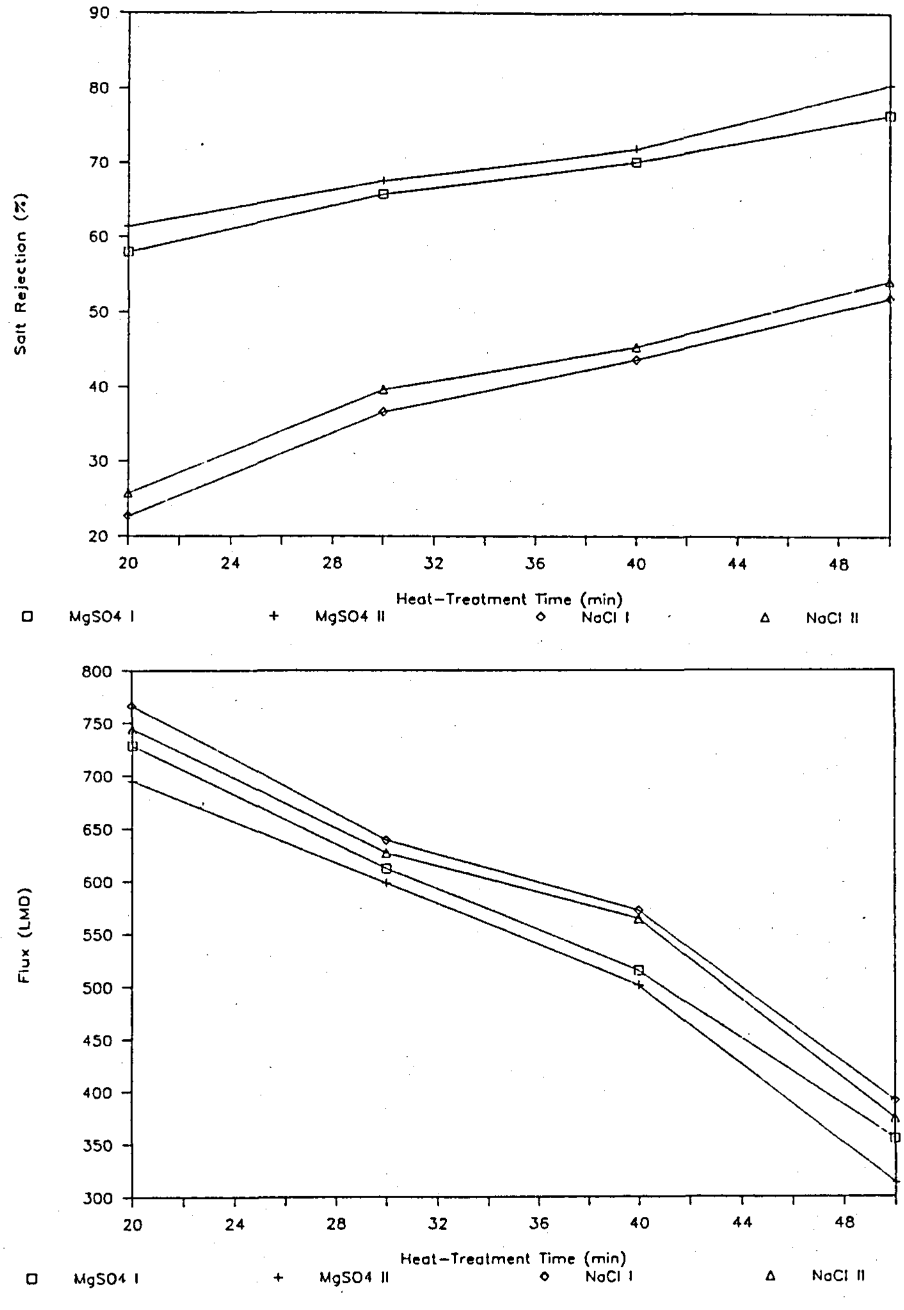


FIGURE 15:

Effect of heat treatment on the RO performance of PVOH/$K_2S_2O_8$ flat-sheet membranes, tested with $MgSO_4$ and NaCl feed solutions. (Series 1 and 2)

From Figures 12 and 13 can be seen the effect of heat-treatment on $MgSO_4$ rejection. Longer heat-treatment periods resulted in higher salt-rejections (as expected). The $MgSO_4$ rejections, after an operating time of 21 hours, were approximately 58 - 61% for membranes which were heat-treated for 20 min, 63 - 65% for membranes which were heat-treated for 30 min, 67 - 69% for membranes which were heat-treated for 40 min, and 75 - 80% for membranes which were heat-treated for 50 min. The water flux decreased from about 700 lmd to between 300 and 400 lmd when the heat-treatment time was increased from 20 min to 50 min.

For all membranes tested, the rejection increased with increasing operating time (Figure 14), and the water flux also increased slightly with increasing operating time. In Figure 15, the NaCl and $MgSO_4$ rejections of membranes heat-treated for different periods of time are compared. The NaCl rejections exhibited by these PVOH/$K_2S_2O_8$ membranes were much lower than the $MgSO_4$ rejections. NaCl rejections of these particular membranes ranged from about 25% to about 50%. There was not much difference between the water fluxes when the feed solution as changed from $MgSO_4$ to NaCl. The fluxes were slightly higher when membranes were tested on a NaCl feed solution.

The reverse osmosis properties of membranes prepared from Solutions 1 and 2 are shown in Tables 38 and 39, respectively. (The formulations and fabrication conditions were summarized in Table 37.)

TABLE 38:

Reverse osmosis properties of flat-sheet PVOH/$K_2S_2O_8$ membranes prepared from Solution 1

Membrane	1	2	3	4	5	6
23,4 hours						
* Rejection (%)	67,5	67,3	64,1	58	66,1	68,4
* Flux (lmd)	735	714	748	798	728	690
94,3 hours						
* Rejection (%)	69.8	68.9	67,1	64,1	68,5	71,2
* Flux (lmd)	718	698	730	761	703	676
149.2 hours						
* Rejection (%)	70,1	70.3	69.2	67.1	69.5	71,8
* Flux (lmd)	724	706	738	774	708	682
168.1 hours						
* Rejection (%)	70,1	70,2	69,4	67,8	69.6	72,0
* Flux (lmd)	722	700	730	765	706	678

* Membranes tested at 2 MPa, 20°C and pH 6.5 on a 1000 mg/ℓ $MgSO_4$ feed solution.

Table 38 shows that membranes prepared from Solution 1 (2% PVOH, MM 72 000; 0,5% $K_2S_2O_8$) exhibited $MgSO_4$ rejections of about 70% and water fluxes exceeding 700 lmd when tested at 2 MPa. The rejection increased with increasing operating time, and the average rejection after an operating time of 168 hours was 69,9%. The fluxes initially decreased and then began to increase again. The water flux had apparently stabilized after an operating time of 168 hours. The average water flux, after 168 hours, was 717 lmd.

TABLE 39:

Reverse osmosis properties of flat-sheet PVOH/$K_2S_2O_8$ membranes prepared from Solution 2

Membrane	1	2	3	4	5	6
21,3 hours						
* Rejection (%)	57,9	51,7	55,8	53,7	59,1	63,6
* Flux (lmd)	605	754	736	595	610	711
93,2 hours						
* Rejection (%)	68,7	62,4	66,8	66,5	69,2	71,4
* Flux (lmd)	518	699	596	478	536	652
146 hours						
* Rejection (%)	71,9	66,5	69,4	71,6	72,0	72,7
* Flux (lmd)	532	716	623	483	553	667
166,2 hours						
* Rejection (%)	72,8	66,9	69,7	71,3	72,2	72,8
* Flux (lmd)	523	714	618	477	550	661
192,9 hours						
* Rejection (%)	38,6	36,9	37,6	43,1	46,7	43,1
* Flux (lmd)	537	702	624	492	590	699
214,1 hours						
* Rejection (%)	38,5	36,6	37,0	43,4	46,7	43,4
* Flux (lmd)	545	718	626	500	597	712
237,1 hours						
* Rejection (%)	38,4	36,2	36,3	43,3	45,6	43,7
* Flux (lmd)	544	721	630	499	600	711

* Tested at 2 MPa, 20°C amd pH 6,5 on a 1000 mg/ℓ $MgSO_4$ solution;
** Tested at 2 MPa, 20°C and pH 6,5 on a 2000 mg/ℓ NaCl solution.

The $MgSO_4$ rejections of membranes prepared from Solution 2 increased with increasing operating time. The average $MgSO_4$ rejection, after 166 hours, was 71%. The average water flux, after 166 hours, was 590 lmd. Both the $MgSO_4$ rejection and the water flux had apparently stabilized after 166 hours of testing. Table 39 shows that the NaCl rejections of these membranes were considerably lower than the $MgSO_4$ rejections. The average NaCl rejection obtained with these membranes was 40,5% (after 49 hours on a NaCl feed solution). When membranes were run on a NaCl feed solution, the fluxes were not much higher than those obtained with $MgSO_4$ as the feed solution (618 lmd for NaCl solution and 590 lmd for $MgSO_4$ solution).

Solution 3 and 4 were prepared from a fully hydrolyzed grade of PVOH (MM 115 000). Since the polymer was insoluble in cold water, the solutions were heated in a boiling water bath until the polymer was completely dissolved. This heating process resulted in discolouration of the solutions and it was also evident that a certain amount of crosslinking had occurred upon heating. In the case of Solution 3, a thick, crosslinked PVOH film was formed. This film, which floated on the surface of the solution, was removed, deposited on a PES support and dried in air at room temperature for a few days. The dried film was very tough and it adhered well to the PES support. Pieces of the film were removed from the support and were immersed in water. The films were swollen to a high degree, but they did not dissolve in water.

In the case of Solution 4, heating in a water bath resulted in a very viscous solution with a red-brown colour. Lumps of crosslinked gel were present in the solution. Since it was clear that heating of these PVOH/$K_2S_2O_8$ solutions resulted in some degree of crosslinking, fresh polymer solutions, without $K_2S_2O_8$ present, were prepared. Solutions were heated in a boiling water bath to dissolve the PVOH, and were then allowed to cool before addition of the appropriate amounts of $K_2S_2O_8$. All the solutions were filtered through a Buchner funnel before being used for membrane preparation. It was extremely difficult to filter Solutions 3 and 4, since the filter paper was blocked very quickly. It is suggested that, in future, a vacuum pump be used to filter such viscous solutions.

The reverse osmosis properties of membranes subsequently prepared from Solutions 3 and 4 are shown in Tables 40 and 41, respectively.

TABLE 40:

Reverse osmosis properties of flat-sheet PVOH/$K_2S_2O_8$ membranes prepared from Solution 3

Membrane	1	2	3	4	5	6
20,8 hours						
* Rejection (%)	65,7	69,1	62,6	68,9	70,1	67,0
* Flux (lmd)	668	637	688	662	623	644
42,6 hours						
* Rejection (%)	66,8	70,3	64,6	69,2	71,5	67,8
* Flux (lmd)	653	622	677	660	608	638

* Tested at 2 MPa, 20°C and pH 6,5 on a 1000 mg/ℓ $MgSO_4$ solution.

TABLE 41:

Reverse osmosis properties of flat-sheet PVOH/$K_2S_2O_8$ membranes prepared from Solution 4

Membrane	1	2	3	4	5	6
22,4 hours						
* Rejection (%)	59,8	68,1	70,6	67,9	70,2	62,2
* Flux (lmd)	592	511	493	516	488	521
46,8 hours						
* Rejection (%)	64,1	68,8	70,8	68,3	71,2	68,4
* Flux (lmd)	566	491	479	503	480	508

* Membranes tested at 2 MPa, 20°C and pH 6,5 on a 1000 mg/ℓ $MgSO_4$ solution.

The average rejections and fluxes of membranes (6 per set) prepared from Solutions 1 to 4 are compared in Table 42.

TABLE 42:

Comparison of average reverse osmosis properties[1] of PVOH/$K_2S_2O_8$ membranes prepared from Solutions 1 to 4

Solution[2]	1	2	3	4
$MgSO_4$ Rejection (%)	69,9	71,0	68,4	68,6
Flux (lmd)	717	590	643	505

1. 2 MPa, 20°C, pH 6,5, 1000 mg/ℓ $MgSO_4$;
2. See Table 37.

Membranes prepared from these solutions exhibited similar salt rejections, but the fluxes varied. The compositions of Solutions 1 and 3 were the same (2% PVOH/0,5%, $K_2S_2O_8$), but the solutions differed with respect to the type and molecular mass of PVOH that was used. Solution 1 contained partially hydrolyzed PVOH with a molecular mass of 72 000, and Solution 3 contained fully hydrolyzed PVOH with a molecular mass of 115 000. Membranes prepared from Solution 1 exhibited higher water fluxes than membranes prepared from Solution 3. This indicated that an increase in molecular mass and degree of hydrolysis of PVOH resulted in a decrease in flux. The same effect was observed when membranes prepared from Solutions 2 and 4 were compared. The level of $MgSO_4$ rejection was the same, but membranes prepared from fully hydrolyzed PVOH (Solution 4) exhibited lower permeate flux.

When membranes prepared from Solution 1 (2% partially hydrolyzed PVOH) and Solution 2 (3% partially hydrolyzed PVOH) were compared, it was clear that an increase in polymer concentration resulted in a decrease in membrane water flux. Membranes prepared from Solution 4 (3% fully hydrolyzed PVOH) also exhibited lower fluxes than membranes prepared from Solution 3 (2% fully hydrolyzed PVOH).

PVOH/$K_2S_2O_8$ flat-sheet membranes were also prepared from a low-molecular mass, fully hydrolyzed grade of PVOH. The membrane coating solution (No. 5) consisted of 4% PVOH (MM 14 000) and 0,5% $K_2S_2O_8$. A few drops of Triton X-100 were added to the solution in an attempt to obtain better wetting of the support membrnae. The following fabrication conditions were used in the making of membranes from Solution 5:

Support predrainig time:	2 min;
Wetting time:	5 min;
Draining time:	2 min;
Curing time;	10 min;
Curing temperature:	110°C.

The low-molecular mass PVOH/$K_2S_2O_8$ membranes exhibited very poor NaCl rejections (< 20%). The water fluxes through these membranes were also surprisingly low (< 2000 lmd). Considering the low NaCl rejection capability, much higher fluxes were expected. A possible explanation could be that the low-molecular mass PVOH actually penetrated the pores of the support membrane to a certain extent and that the polymer was crosslinked inside the pores during heat treatment. Such a pore-blocking effect could result in the low water fluxes. No further work was done on low MM PVOH membranes.

Tubular membranes

PVOH/$K_2S_2O_8$ coating were also deposited on tubular PES support membranes (M 719) and cured by heat treatment. The compositions of the coating formulations and the fabrication conditions are summarized in Table 43. The effects of pH, operating pressure and heat-treatment on reverse osmosis properties of tubular PVOH/$K_2S_2O_8$ membranes were studied. The rejection and flux values reported represent the average of 4 measured values (4 membranes prepared from each solution).

TABLE 43:

Compositions of coating solutions and membrane fabrication conditions:
Tubular PVOH/$K_2S_2O_8$ membranes

Membrane code Coating Solution No.	MEM1/PH[3] 1	MEM2/PH[3] 2	MEM3/FH[3] 3	MEM4/FH[3] 4
PVOH[1] (mass %)	2	3	-	-
PVOH[2] (mass %)	-	-	2	3
$K_2S_2O_8$ (mass %)	0.5	1,0	0,5	1,0
Support predraining time (min)	2	2	2	2
Wetting time (min)	5	5	5	5
Draining time (min)	1	1	1	1
Curing time (min)	10	10	10	10
Curing temperature (°C)	100	100	100	100

1. PVOH MM 72 000, partially hydrolyzed (SAARCHEM);
2. PVOH MM 115 000, fully hydrolyzed (ALDRICH);
3. PH = partially hydrolyzed PVOH; FH = fully hydrolyzed PVOH.

The effect of pH on reverse osmosis properties of tubular PVOH/$K_2S_2O_8$ membranes (prepared from Solutions 1 to 4) is shown in Table 44. Generally, the $MgSO_4$ rejection increased with increasing pH of the feed solution (pH 3 —— pH 7 —— pH 10).

TABLE 44:

Reverse osmosis properties[1] of tubular PVOH/$K_2S_2O_8$ membranes[2] at different pH values

Membrane	MEM1/PH	MEM2/PH	MEM3/FH	MEM4/FH
pH 3				
Rejection (%)	25.1	18,1	26,6	21,7
Flux (lmd)	210	184	155	241
pH 7				
Rejection (%)	25.1	26.0	38,5	30.9
Flux (lmd)	228	263	153	231
pH 10				
Rejection (%)	27,8	22,8	42,8	38,3
Flux (lmd)	243	253	142	211

1. Membranes tested at 0.5 MPa and 20°C on a 1000 mg/ℓ $MgSO_4$ feed solution;
2. MEM1/PH: 2% PH PVOH, 0.5% $K_2S_2O_8$; MEM2/PH: 3% PH PVOH, 1% $K_2S_2O_8$; MEM3/FH: 2% FH PVOH, 0.5% $K_2S_2O_8$; MEM4/FH: 3% FH PVOH, 1% $K_2S_2O_8$.

The effect of operating pressure on the reverse osmosis properties of tubular PVOH/$K_2S_2O_8$ membranes is shown in Table 45.

TABLE 45:

Reverse osmosis properties[1] of tubular PVOH/$K_2S_2O_8$ membranes[2] at different operating pressures

Membrane	MEM1/PH	MEM2/PH	MEM3/FH	MEM4/FH
0.5 MPa				
Rejection (%)	30.6	26.9	40,7	31,7
Flux (lmd)	205	215	156	273
1 MPa				
Rejection (%)	45,6	39,5	58,1	47,3
Flux (lmd)	498	547	334	440
1,5 MPa				
Rejection (%)	52,3	45,1	59.8	45,5
Flux (lmd)	836	849	579	812
2 MPa				
Rejection (%)	54,5	47,4	64,3	49,3
Flux (lmd)	1078	1014	749	1022

1. Membranes tested at 20°C and pH 6,4 on a 1000 mg/ℓ $MgSO_4$ feed solution;
2. MEM1/PH: 2% PH PVOH, 0,5% $K_2S_2O_8$: MEM2/PH 3% PH PVOH, 1% $K_2S_2O_8$; MEM3/FH: 2% FH PVOH, 0,5% $K_2S_2O_8$; MEM4/FH: 3% FH PVOH, 1% $K_2S_2O_8$.

Table 45 shows that both the salt rejection and the flux increased with increasing operating pressure (as expected). Membranes prepared from 2% fully hydrolyzed PVOH (MEM3/FH) exhibited the highest $MgSO_4$ rejection and the lowest water flux at 2 MPa. The water fluxes of these membranes at 2 MPa were quite high, and the reverse osmosis properties were generally promising. It was also noted that the rejections of membranes prepared from fully hydrolyzed PVOH (MEM3/FH and MEM4/FH) did not increase significantly when the pressure was increased from 1 MPa to 2 MPa. Contrary to the rejection behaviour, these membranes exhibited large increases in water flux with increasing operating pressure.

The effect of heat-treatment time on reverse osmosis properties of MEM1/PH (prepared from Solution 1: 2% PVOH; 0,5% $K_2S_2O_8$) was studied as a function of operating pressure and operating time. The membrane fabrication conditions were:

Support predraining time:	2 min;
Wetting time:	5 min;
Draining time:	1 min;
Curing temperature:	90°C;
Curing times:	5, 10, 15 or 20 min.

The results of this experiment are shown in Figures 16 and 17.

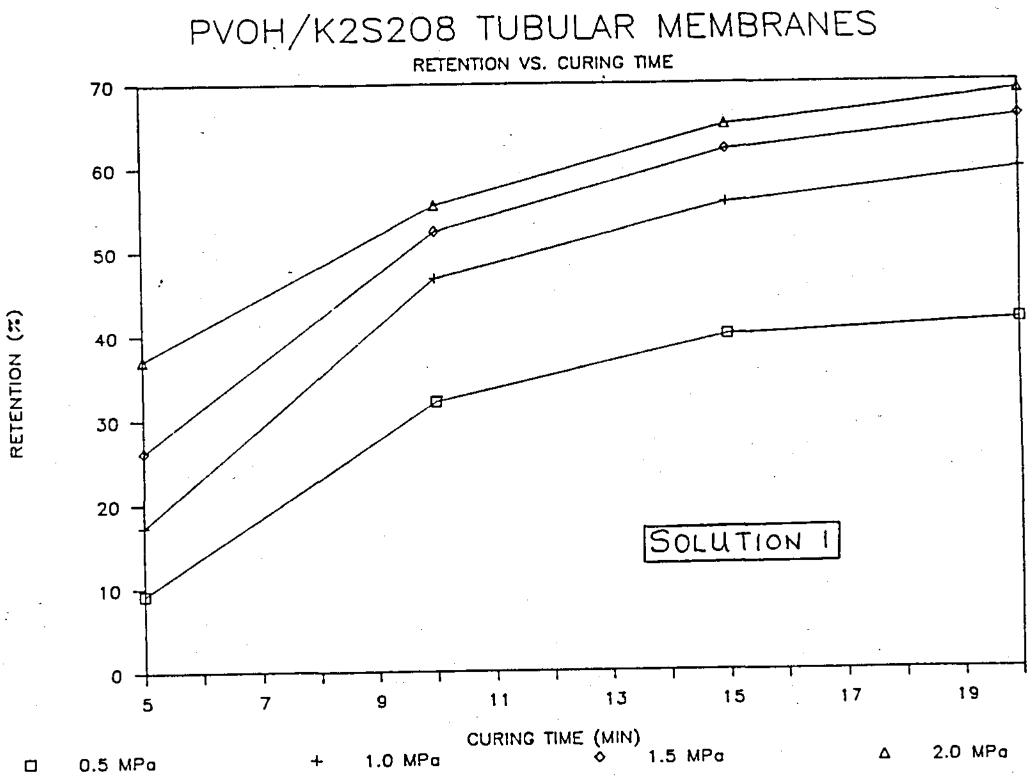


FIGURE 16:
PVOH/$K_2S_2O_8$ tubular membranes: Retention v/s curing time, tested at different pressures

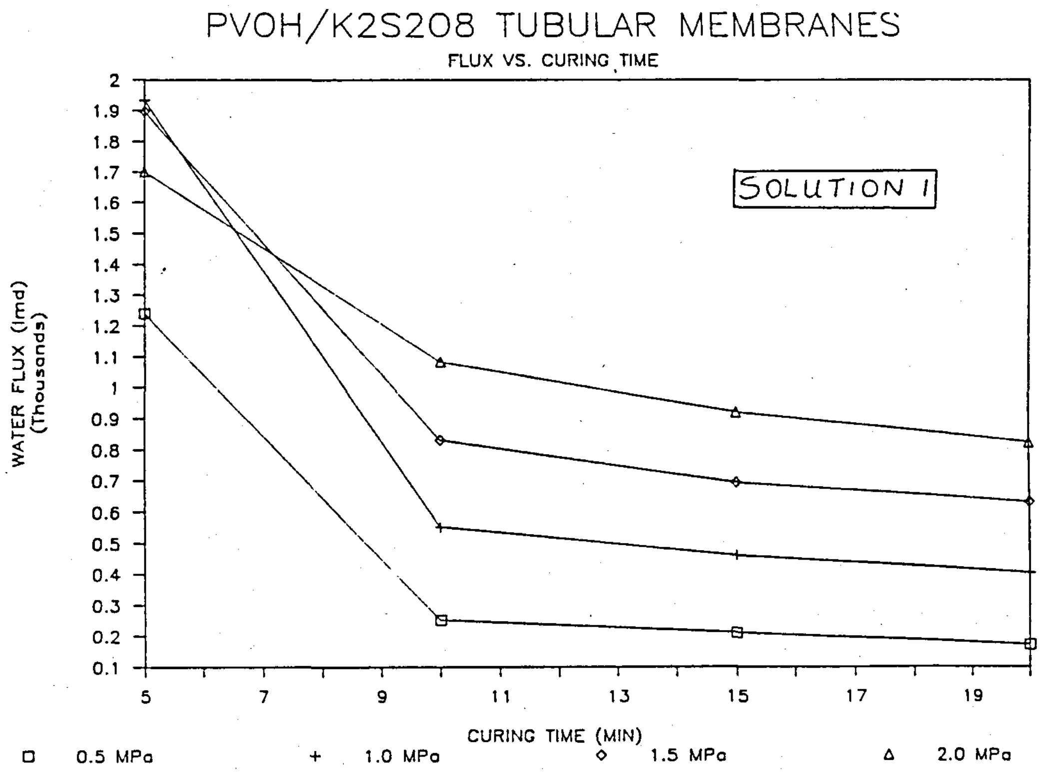


FIGURE 17:
PVOH/$K_2S_2O_8$ tubular membranes: Flux v/s curing time, tested at different pressures

Figure 16 shows the $MgSO_4$ rejection as a function of curing time. It can be seen that, at all operating pressures, the rejections increased with increasing curing time. Membranes cured for 5 min exhibited rejections of 9% at 0,5 MPa and 37% at 2 MPa. When membranes were cured for 20 min, the rejections increased to 41% at 0,5 MPa and 69% at 2 MPa. The water fluxes at different operating pressures decreased with increasing curing time, as shown in Figure 17. The decrease in flux as a function of curing time was particularly significant when membranes were heat-treated for 10 min instead of 5 min. The fluxes of membranes heat-treated for 5 min were 1250 lmd at 0,5 MPa and 1700 lmd at 2 MPa. When membranes were heat-treated for 20 min, the fluxes decreased to 171 lmd at 0,5 MPa and 823 lmd at 2 MPa.

Tubular PVOH/$K_2S_2O_8$ membranes exhibited a more widespread variation of salt rejection and flux properties than flat-sheet membranes did. The results obtained with tubular membranes were also more inconsistent. In spite of the variations in membrane properties, the results recorded were considered as being quite promising. A thorough study of all the formulation and fabrication variables is required to optimize the RO properties of these membranes. Analytical studies are also required in order to obtained information about the crosslinking mechanism and the chemical nature of the crosslinked membranes.

Possible mechanisms for the crosslinking of PVOH membranes in the presence of persulphate are currently being studied.

5.4.2.10 Membranes prepared by interfacial crosslinking of PVOH

Attempts were made to prepare PVOH membranes by interfacial crosslinking with di- and triacid chlorides. The preparation of RO membranes by interfacial crosslinking of polyhydroxy compounds has been discussed in an European Patent (EP O 227 042 A) **[19]**. The membrane coating formulations discussed in this patent also contained polyamine compounds. The interfacially crosslinked PVOH membranes investigated at IPS, and reported here, contained no amine compounds.

The aqueous phase consisted of a 50 : 50 mixture of a 2% aqueous solution of PVOH (MM 125 000) and a 4 M NaOH solution. The organic phase consisted of 0,2% isophthaloyl chloride (IPC) in hexane. Membranes were prepared by immersing the PES support in the aqueous phase for 5 min, draining the membrane for 1 min at room temperature, drying it for 10 min at 50°C, and immersing it in the organic phase for 1 min. Membranes were heat-treated for 10 min at 110°C.

The results obtained with these membranes are shown in Table 46.

TABLE 46:
Reverse osmosis properties[1] of interfacially crosslinked PVOH membranes (flat-sheets)

Membrane	1	2	3	4
pH 6.6				
Rejection (%)	4,4	5,4	5,2	5,0
Flux (lmd)	358	477	159	150
pH 10				
Rejection (%)	7,2	7,2	6,6	7,6
Flux (lmd)	309	445	173	157
pH 3				
Rejection (%)	2,8	3,7	4,4	4,8
Flux (lmd)	4056	4891	1688	1434

1. Membranes tested at 2 MPa and 20°C on a 2000 mg/ℓ NaCl feed solution.

These interfacially crosslinked PVOH membranes exhibited very poor RO properties; the low water fluxes at pH 6,6 and pH 10 would usually indicate that a high degree of crosslinking had occurred. It this was so, the membranes should have exhibited relatively high salt rejections. Table 46 shows that these membranes had virtually no NaCl rejection capability when tested at 2 MPa. The drastic increase in water flux at pH 3 is also difficult to explain. It can be assumed that drying of the membranes at 50°C before immersing them in the crosslinking solution resulted in very dense membranes and, consequently, very low fluxes. No explanation can be offered for the low NaCl rejections which accompanied threse low water fluxes. No further work was done on these membranes.

5.4.3 PVOH-COATED UF MEMBRANES TESTED ON SASOL EFFLUENT

Uncoated UF membranes (batch code 545 T), as well as PVOH-coated 545T UF membranes, were tested on Sasol effluent. Permeate fluxes were measured at 20°C and an operating pressure of 200 kPa. In the case of the uncoated membranes: after an operating time of 6,4 hours at 200 kPa, 5 litres of permeate were withdrawn and stored and after 20,95 hours, another 5 l volume of permeate was withdrawn and stored. RO performance of the membranes on the reduced volume of feed solution were recorded. The 10 litres of permeate collected during the test were again added to the feed solution after a running time of 26,5 hours and RO performance again recorded. The variation of permeate flux with operating time was monitored over a period of 27,5 hours. The results of this test for 6 membranes are shown in Figure 18. Although the flux decreased with time due to fouling, the flux values obtained after removal of 10 l permeate were higher than 350 LMD at 200 kPa. After adding the 10 l permeate, the fluxes increased again.

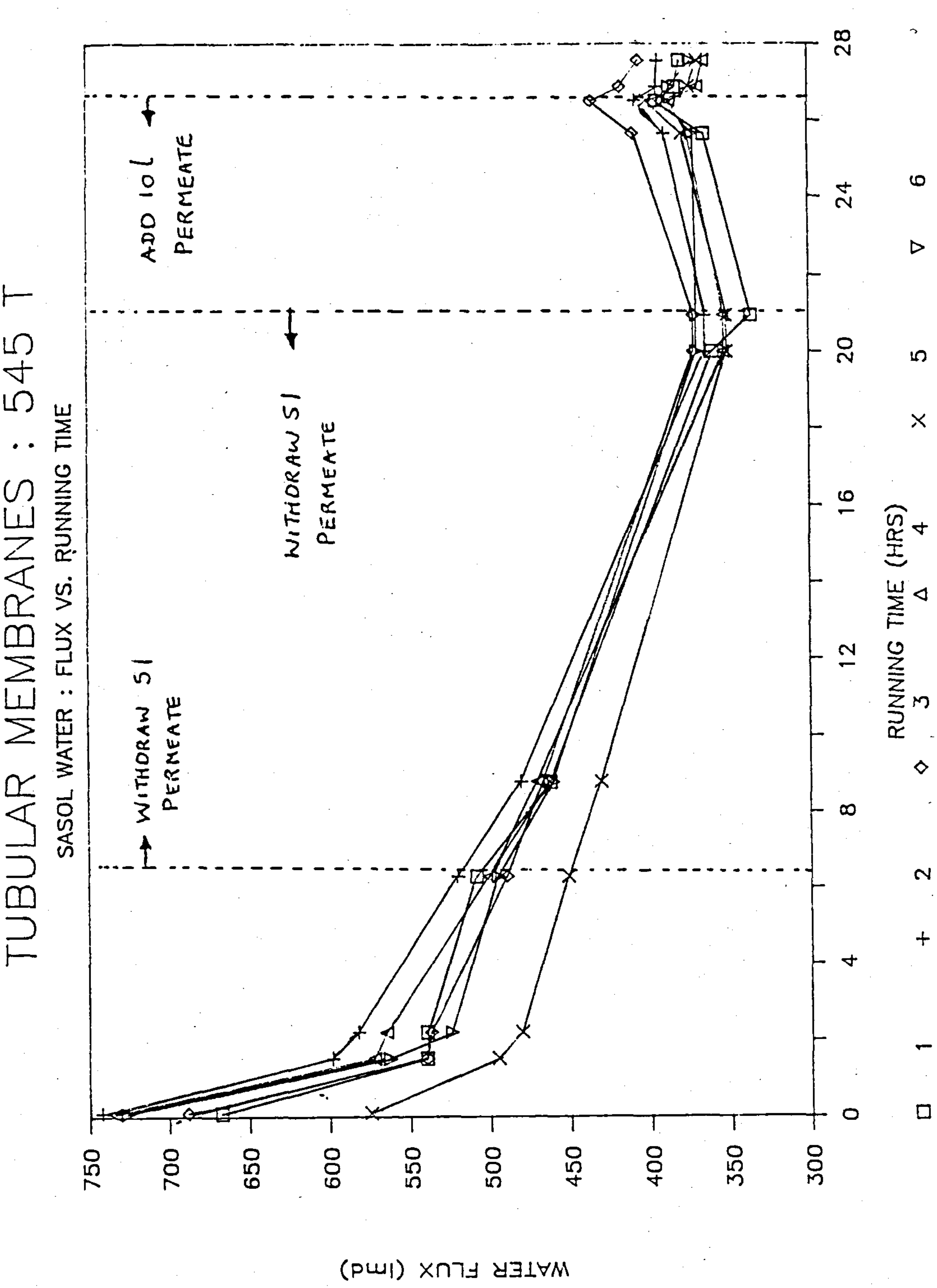


FIGURE 18:
Results of tubular UF membranes (545 T) tested on Sasol water: Flux v/s operating time

The 545T UF membranes were then coated with a solution containing 2% partially hydrolyzed PVOH and 0,5% $K_2S_2O_8$. The UF membranes were predrained for 2 min and wetted in the PVOH solution for 2 min. These membranes were not heat-treated, but were air-dried for 60 min. The variation of permeate flux with operating time was studied. After 18,8 hours, 5 litres of permeate were withdrawn. The permeate flux was monitored for a period of 40,8 hours. The results of this test are shown in Figure 19 (6 membranes). The initial increase in permeate flux was probably due to dissolution of the uncrosslinked PVOH coating.

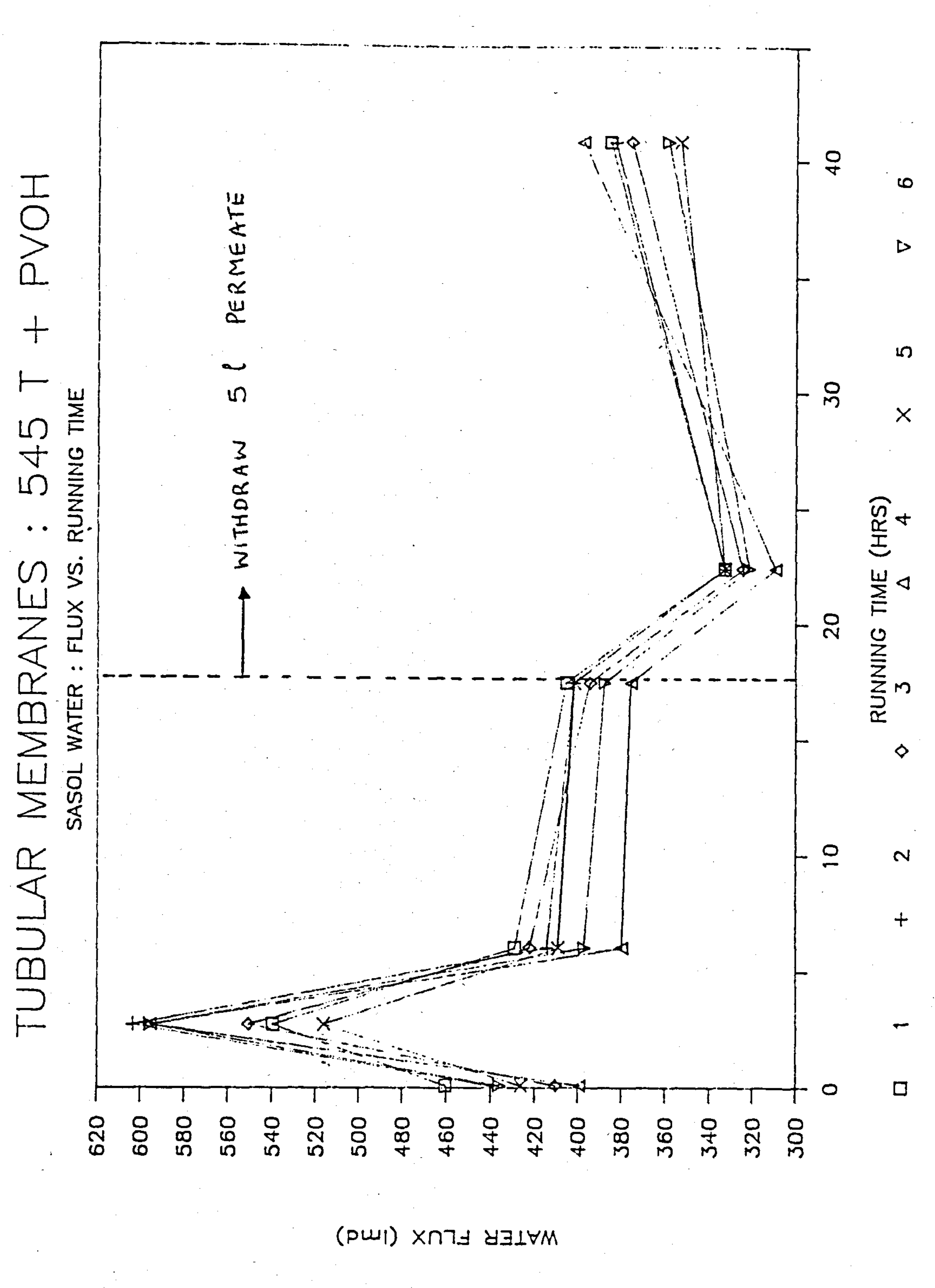


FIGURE 19:

Results of tests of tubular membranes: 545 T + PVOH with Sasol water: Flux v/s running time

5.4.4 INTERFACIAL SYNTHESIS

The following reactions were investigated:

(a) Reaction of PVOH (aqueous phase) with acid chlorides (organic phase) - crosslinking by ester-bond formation;

(b) Reaction of mixtures of PVOH and other hydroxy compounds (acqueous phase) with acid chlorides (organic phase) - crosslinking of PVOH by ester-bond formation, and possibly polycondensation of hydroxy compounds with acid chlorides;

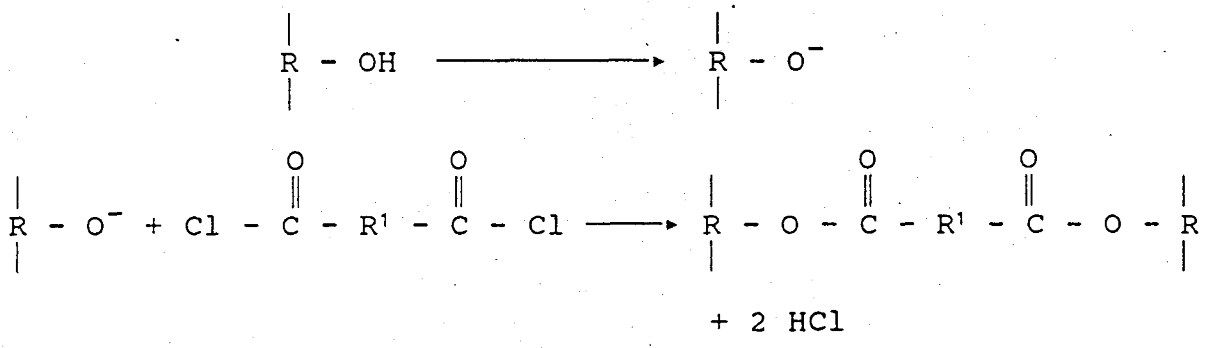
(c) Reaction of multifunctional hydroxy compounds (aqueous phase) with acid chlorides (organic phase) - synthesis of polyester by interfacial polycondensation;

(d) Reaction of PVOH (acqueous phase) with the difunctional halide α, α^1- dichloro-p-xylene (organic phase) - crosslinking of PVOH by ether-bond formation;

(e) Reaction of multifunctional hydroxy compounds (aqueous phase) with α, α^1-dichloroxylene (organic phase) - synthesis of polyether by interfacial polycondensation.

Reaction (a) has been used to prepare PVOH membranes, but the RO properties of the resulting membranes were very poor (Section 5.4.2.10). Reactions (b) to (e) have, as yet, not been applied to the formation of UTF RO membranes. All experiments were first conducted in polytops or small glass beakers; the objective being to determine whether any reaction occurred when solutions containing the different components were brought into contact with each other.

Addition of hexane solutions of di- and triacid chlorides to aqueous alkaline PVOH solutions resulted in the instantaneous formation of very thin, but visible, films (or layers of precipitated polymer) at the interface between the aqueous and organic layers. This film formation indicated that some degree of crosslinking had occurred. PVOH solutions having different concentrations were used in these investigations. The acid chlorides used were isophthaloyl chloride (IPC), terephthaloyl chloride (TPC) and trimesoyl chloride (TMC). In all cases, an equivalent volume of NaOH solution (4 M) was added to the aqueous PVOH solutions before contacting the aqueous phase with the organic phase. Addition of NaOH is important, since its role is to convert the hydroxyl groups to alkoxide groups (RO-), which act as the reactive species. NaOH also acts as acid acceptor, to neutralize free acid which is formed during the reaction of acid chlorides/hydrolysis of acid chlorides.



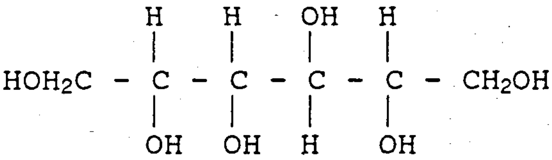
$$\overset{|}{\underset{|}{R}} - OH \longrightarrow \overset{|}{\underset{|}{R}} - O^-$$

$$\overset{|}{\underset{|}{R}} - O^- + Cl - \overset{O}{\overset{\|}{C}} - R^1 - \overset{O}{\overset{\|}{C}} - Cl \longrightarrow \overset{|}{\underset{|}{R}} - O - \overset{O}{\overset{\|}{C}} - R^1 - \overset{O}{\overset{\|}{C}} - O - \overset{|}{\underset{|}{R}} + 2\,HCl$$

It has been reported **[20]** that - in contrast to the effect of alkali in the interfacial polycondensation of dicarboxylic acid chlorides with diphenols, where a small excess produced a molecular mass reduction of the polyester and a decrease in its yield - an increase in alkali concentration in the aqueous phase during interfacial esterification of PVOH increased esterification efficiency. A NaOH concentration of about 4 M is usually employed in these reactions.

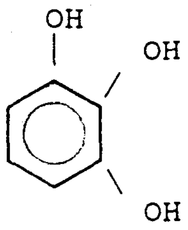
Film-formation at the interface was also observed when aqueous solutions containing both PVOH and multifunctional hydroxy compounds were contacted with a hexane solution of the acid chloride. The hydroxy compounds used in these investigations were:

Sorbitol

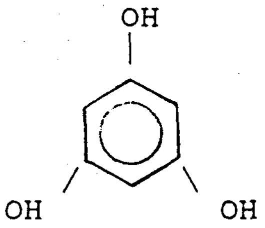


$$\mathrm{HOH_2C} - \underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}} - \underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}} - \underset{\mathrm{H}}{\overset{\mathrm{OH}}{\mathrm{C}}} - \underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}} - \mathrm{CH_2OH}$$

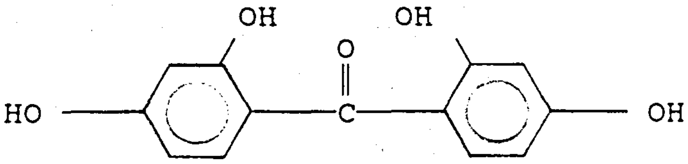
Pyrogallol



Phloroglucinol



and 2,2,4,4-tetrahydroxybenzophenone



In polycondensation reactions, where the hydroxy compounds alone are used in the aqueous phase (without PVOH), the proportion of the NaOH (or other acid acceptor) is quite critical. In this type of reaction, the use of an equimolar amount of the acid acceptor will probably produce the best results.

The solubility of the organic solvent in water is an important factor in the interfacial esterification/crosslinking of PVOH. Very good results are usually obtained (in the esterification of PVOH) when the acid chloride is dissolved in methylene dichloride, while solvents such as chlorobenzene give poor yields. This means that the organic solvent used in the process is required to have a certain solubility in the water layer. PVOH has no solubility in organic solvents; therefore, the mechanism of polyamide and polyester interfacial polycondensation suggested by Morgan **[21]**, i.e., that the reaction proceeds by the diffusion of diamines or diols from the water layer into the organic solvent layer, can not be applied in the case of PVOH. In the interfacial esterification of PVOH, the reaction should be considered to begin in the water layer and to proceed by the diffusion of acid halide, dissolved in the organic phase, across the interface and into the water phase.

In membrane preparations, only solvents which will not damage the PES support can be used. This severely limits the possibilities, and also the efficiency of interfacial reactions. Methylene dichloride, MEK, petroleum ether, cyclohexanone and tetrahydrofuran are commonly used in interfacial esterification of PVOH. None of these solvents can be used in membrane preparations on PS supports.

Attempts to crosslink PVOH by means of an interfacial etherification reaction, using α, α^1-dichloro-p-xylene as crosslinking agent, were unsuccessful. No film-formation could be observed when the organic solution of the crosslinking agent was poured into an aqueous alkaline solution of PVOH. The aqueous solution consisted of equal volumes of a 2% PVOH solution and a 4 M NaOH solution, and a small amount of tetraethylammonium hydroxide as phase-transfer catalyst. The appropriate experimental conditions for phase-transfer-catalyzed synthesis of polyethers have not been established. This type of reaction will probably not proceed in the case of PVOH, because of the requirement that reagents must be transferred across the interface. Transfer of PVOH (or the alkoxide form of the polymer after reaction with base) across the interface is impossible, not only because of the size of the molecule, but also because the polymer is insoluble in the organic solvents which are used to dissolve the alkyl or aryl halide. The phase-transfer-catalyzed interfacial synthesis of polyethers from aromatic diols/triols and aryl dihalides is possible, and this type of reaction could be investigated further.

5.4.5 SUMMARY

Resulting from this work, a poster was created "UTF Fixed Membranes formed by Crosslinking or Insolubilization of Poly(vinylalcohol)" and presented at the MTD SAMSIG Conference held at the Wilderness, November 21-22, 1989.

5.5 MEMBRANES MADE FROM HYDROXYL-CONTAINING COPOLYMERS

Materials previously used for dynamic membranes.

5.5.1 INTRODUCTION

Recent research at the Institute on the development of novel polyelectrolytes for the use as dynamic membranes **[22]** led to the synthesis of a large range of poly(acrylic acid-co-vinyl acetate) copolymers. During an investigation into the ability of these polymers to interact with zirconium in acidic medium **[22, 23]** it was noticed that a few of these polymers formed tough, water-insoluble films upon exposure to an acidic solution of zirconium. This led to an attempt to use these polymers, crosslinked by zirconium, as fixed, thin-film membranes.

The two polymers selected for this experiment were not soluble in an acidic medium, so that the crosslinking reaction, as it was done, was virtually an interfacial reaction.

5.5.2 EXPERIMENTAL

Polymerization

The details of the preparation of the acrylic acid-vinyl acetate copolymers have been described previously **[22]** and will not be repeated here.

Reagents

Zirconium solutions were made up from a 1000 mg/ℓ standard obtained from SAARCHEM. Polymers were dissolved in analytical grade methanol (NT laboratories), and the HCl used to make up the acidic zirconium solutions was CP grade (NT laboratories).

Membrane precursor preparation

Two polymers, codes AVAC 17 and AVAC 15, containing 43% and 60% carboxylic acid groups, respectively, was used as membrane precursors. These polymers were dissolved in methanol (1% m/m concentration). The zirconium solution was made up by diluting 50 ml of the 1000 mg/ℓ standard zirconium solution to 1000 ml with aqueous HCl, so that the final HCl concentration was 0,3 mole.dm^{-3}.

Membrane substrates

The membranes substrates were tubular ultrafiltration membranes, comprising polyester paper with a poly(aryl ether sulphone) coating. Membrane substrate configuration was either 13 or 9 mm tubes.

Membrane formation

The membrane substrate was dipped into the precursor solution, drained, then dipped into a 50 mg/ℓ zirconium solution in 0,3 M aqueous HCl. The membrane was drained and then dried in a vertical updraft oven. The membrane codes and manufacture parameters are given in detail in Table 47.

TABLE 47:

Fabrication conditions for AVAC/Zr membranes

Membrane	Precursor	Crosslinking	Substrate	Configuration	Pretreatment
LPA 0	AVAC 15	50 mg/ℓ Zr^{4+}	-	13 mm	-
LPA 1	AVAC 17	50 mg/ℓ Zr^{4+}	9/720[1]	9 mm	-
LPA 2	AVAC 17	50 mg/ℓ Zr^{4+}	9/720	9 mm	-
LPB 1	AVAC 17	50 mg/ℓ Zr^{4+}	519T48G719[2]	13 mm	Tydex[3]
LPB 2	AVAC 17	50 mg/ℓ Zr^{4+}	519T48G719	13 mm	Tydex

1. Membratek 9 mm ("TUF 9") ultrafiltration membrane;
2. Substrate made at the Institute;
3. Substrate dipped for 10 min into a 0,1% solution of Tydex 16 (DOW), a poly(ethylene imine) solution.

Membrane results

The results obtained with the LPA 0 membrane (AVAC 15 precursor) is given in Table 48.

TABLE 48:

Performance of LPA O Type membranes (AVAC/Zr)

Membrane no	Rejection (%)	Flux (lmd)	pH	Solute (1000 mg/ℓ)
1	47,8	1075	6,7	$NaNO_3$
2	54,4	620	6.7	$NaNO_3$
3	34,0	1214	6,7	$NaNO_3$
1	43,4	-	5.0	$NaNO_3$
2	50,9	-	5,0	$NaNO_3$
3	28,1	-	5,0	$NaNO_3$
1	11,8	663	3,0	$NaNO_3$
2	14,8	450	3,0	$NaNO_3$
3	10,6	1000	3,0	$NaNo_3$
1	56,1	820	6,6	$MgSO_4$
2	60,0	565	6,6	$MgSO_4$
3	31,1	744	6,6	$MgSO_4$

It is clear from these results that the carboxylic acid content of these membranes is sufficiently high for the membranes to show a marked response to a change in the pH of the feed solution, and to the presence of divalent cations at neutral or nearly neutral pH. In the light of the above results, all subsequent membranes were made with the AVAC 17 copolymer. The results of these experiments are shown in Figures 20 and 21.

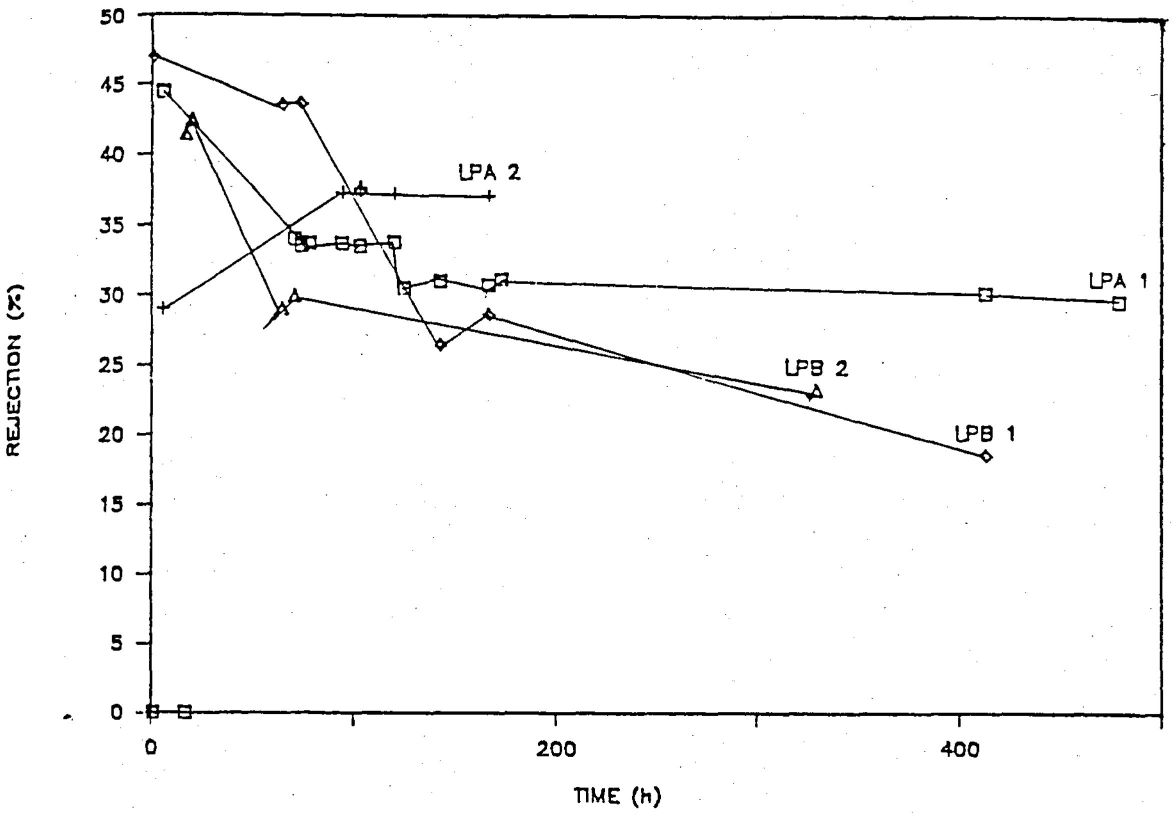


FIGURE 20:
Effect of testing time on rejection of LPA (AVAC/Zr) membranes

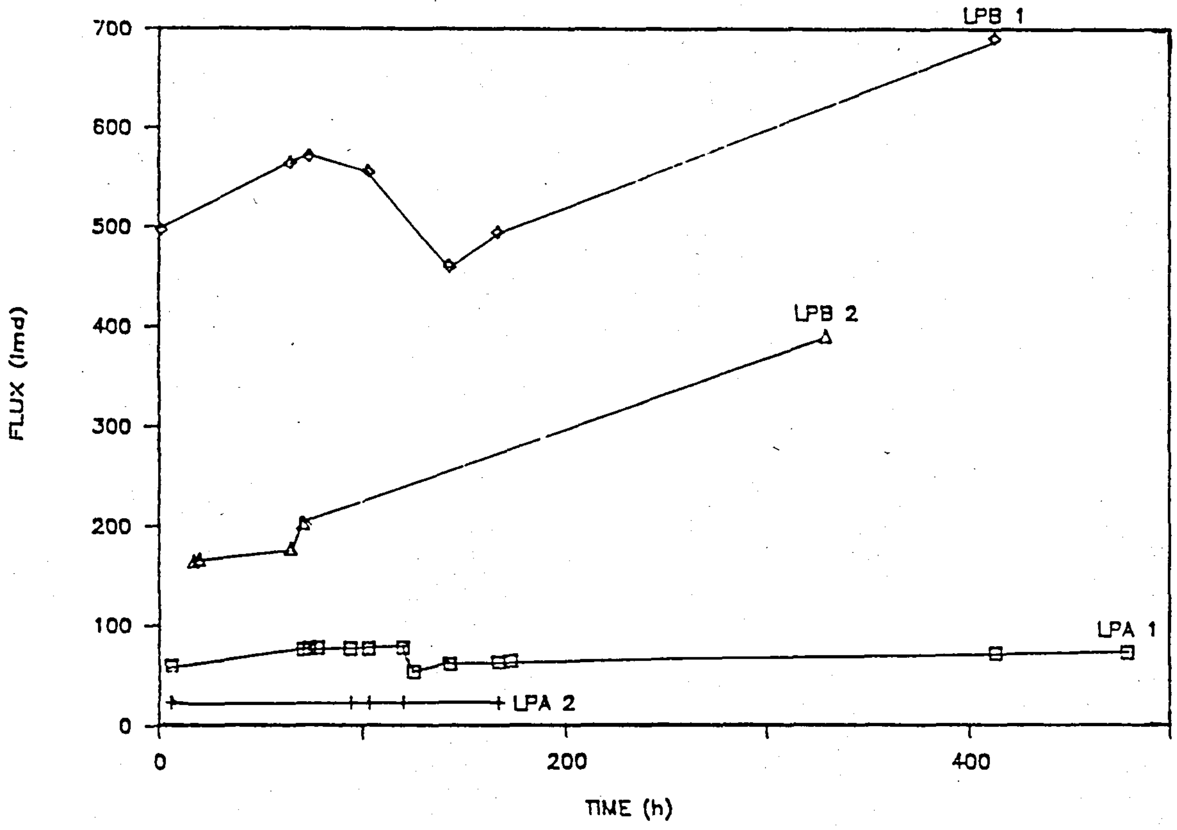


FIGURE 21:
Effect of testing time on flux of LPA (AVAC/Zr) membranes

It is evident that these membranes are not stable over long periods of time, and the fluxes of the membranes formed in the 13 mm tubular substrate are much higher than the fluxes of those membranes formed in the 9 mm substrates. The latter might of course be due to the Tydex treatment, but the fluxes obtained with the AVAC 15 copolymer membranes in 13 mm tubes are also much higher than those obtained on the 9/720 substrates.

5.5.4 CONCLUSIONS

The AVAC 15 and AVAC 17 low pressure membranes are not stable enough to warrant any practical implementation at this stage. Their loss in performance over a long period of time was possibly due to hydrolysis on the vinyl acetate.

5.6 RECOMMENDATIONS

5.7 REFERENCES

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SECTION 3

6. RESEARCH ON THE DEVELOPMENT OF POLYMERS FOR THE FORMATION OF DYNAMIC MEMBRANES AND EVALUATION THEREOF FOR THE TREATMENT OF INDUSTRIAL EFFLUENT

6.1 INTRODUCTION

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 development of alternate polyelectrolytes to supersede poly(acrylic acid).

Research on the development of polymers for dynamic membranes started in 1984 at this Institute and ran virtually continuously until December 1990. For the sake of presenting a complete picture we elected to include here the results of all the research work, from 1984 to 1990. Research at the IPS on dynamic membranes during the period January 1984 to December 1990 can be divided into three separate approaches:

1. The initial stage, January 1984 to December 1985, involved 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 study of the use of poly(acrylic acid-co-vinyl acetate) and poly(acrylic acid-co-vinyl alcohol) as dynamic membrane polyelectrolytes.
3. The third stage, January 1989 to December 1990, which involved the use of poly(acrylic acid-co-hydroxyethyl acrylate) and poly(acrylic acid-co-hydroxymethyl methacrylate) as dynamic membrane polyelectrolytes. These polymers are crosslinkable.

6.2 THE PERIOD JANUARY 1984 TO DECEMBER 1985

The research done at the IPS on dynamic membranes during this period is thoroughly described in the masters theses of Van Reenen [1] and Dowler [2]. A summary of the significant experimental details and results is given below:

6.2.1 BACKGROUND

The research during 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 ionized at neutral pH (see Figure 22), thus giving a membrane that is negatively charged.

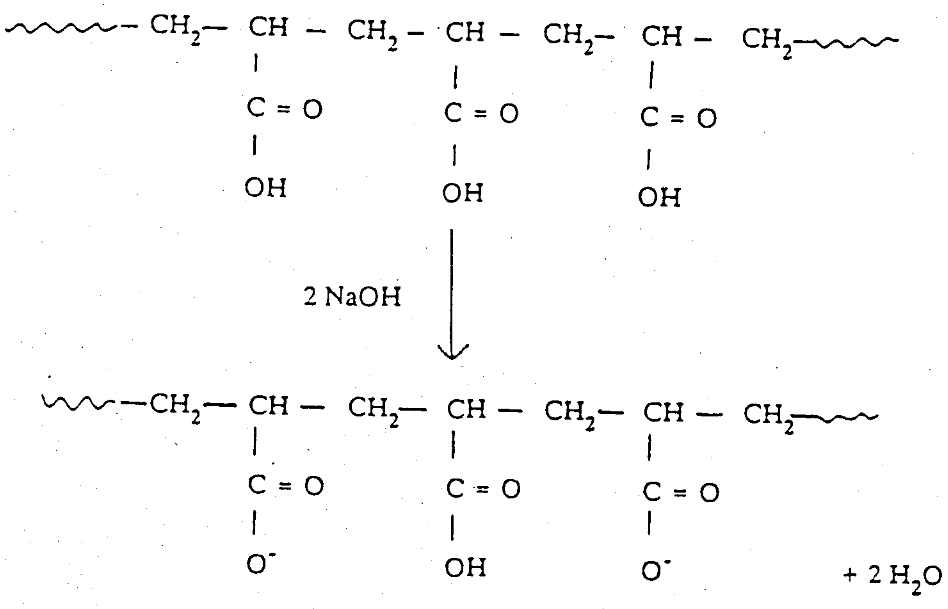


FIGURE 22:
Ionization of poly(acrylic acid)

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.

6.2.2 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

and 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

and the following terpolymer:

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

These polyelectrolytes were used to form dynamic membranes. Membranes were also made from 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 master's theses [1].

The best membrane results obtained with these polyelectrolytes are given in Table 49.

TABLE 49:

Polyelectrolyte characteristics and membrane performance data of dynamic membranes

Polymer code	Composition (Monomer ratio)	Mol. mass	pH 7^1 R (%)	J (lmh)	pH 8 R (%)	J (lmh)	pH 9 R (%)	J (lmh)
PAA	-	75 000	90,4	87	93,2	75	90.2	79
PIA	-	43 200	54,7	423	57,8	423	61,0	400
PCIAA	-	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/CIAA	60/40	95 200	79,2	344	79,8	332	84,5	302
PMAA/CIAA	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 49, none of the more highly charged polyelectrolytes showed any improvement over poly(acrylic acid) in terms of rejection capabilities, although much higher fluxes were obtained. The only membrane to show any improvement over poly(acrylic acid) was 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 (Table 50).

TABLE 50:

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 50, 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 markedly better, though. These results, as with results obtained from the PAA/VAC membranes (see Table 49), indicated that there is a contribution to the salt rejection by dynamically formed polyelectrolyte membranes by the hydrophobic (uncharged) sections of the polyelectrolyte. There were further indications that increasing 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.

6.3 THE PERIOD JANUARY 1986 TO MARCH 1988

6.3.1 BACKGROUND

Van Reenen concentrated in this period of time, on 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. A complete report is given in his Ph.D. thesis [3].

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 have been fully described **[3]**.

6.3.2 RESULTS

The results are divided into three separate sections.

(i) Polymerisation and characterisation.
(ii) Membrane results.
(iii) Results pendant to, and arising from, the original study.

6.3.2.1 Polymerisation and characterisation

Polymerisation. A table giving the many polymerisation mixtures prepared as well as their polymer codes has been compiled (Table 51). Selected AVAC copolymers were hydrolyzed fully to give the poly(acrylic acid-co-vinyl alcohol) copolymers, code-named 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*.

TABLE 51:

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 ($x10^{-1}$)	ml ($x10^2$)	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 only suitable eluent to use in gel permeation chromatography (GPC), THF. The molecular masses obtained with GPC are given in Table 52.

TABLE 52:
Molecular masses 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.

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 during reaction are the deciding factors when it comes to the determination of molecular mass of a polymer.

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 23.

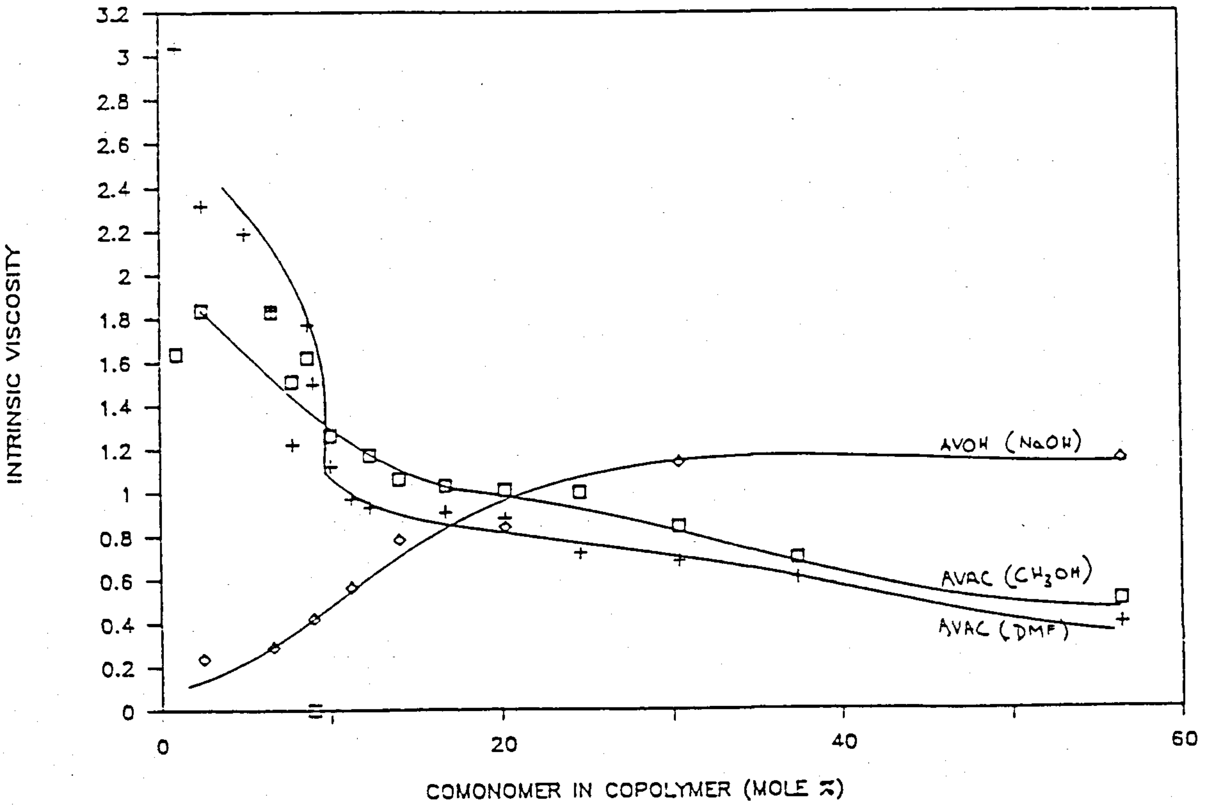


FIGURE 23:
Intrinsic viscosities of co- and terpolymers

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 24 and the composition analysis is given in Table 53.

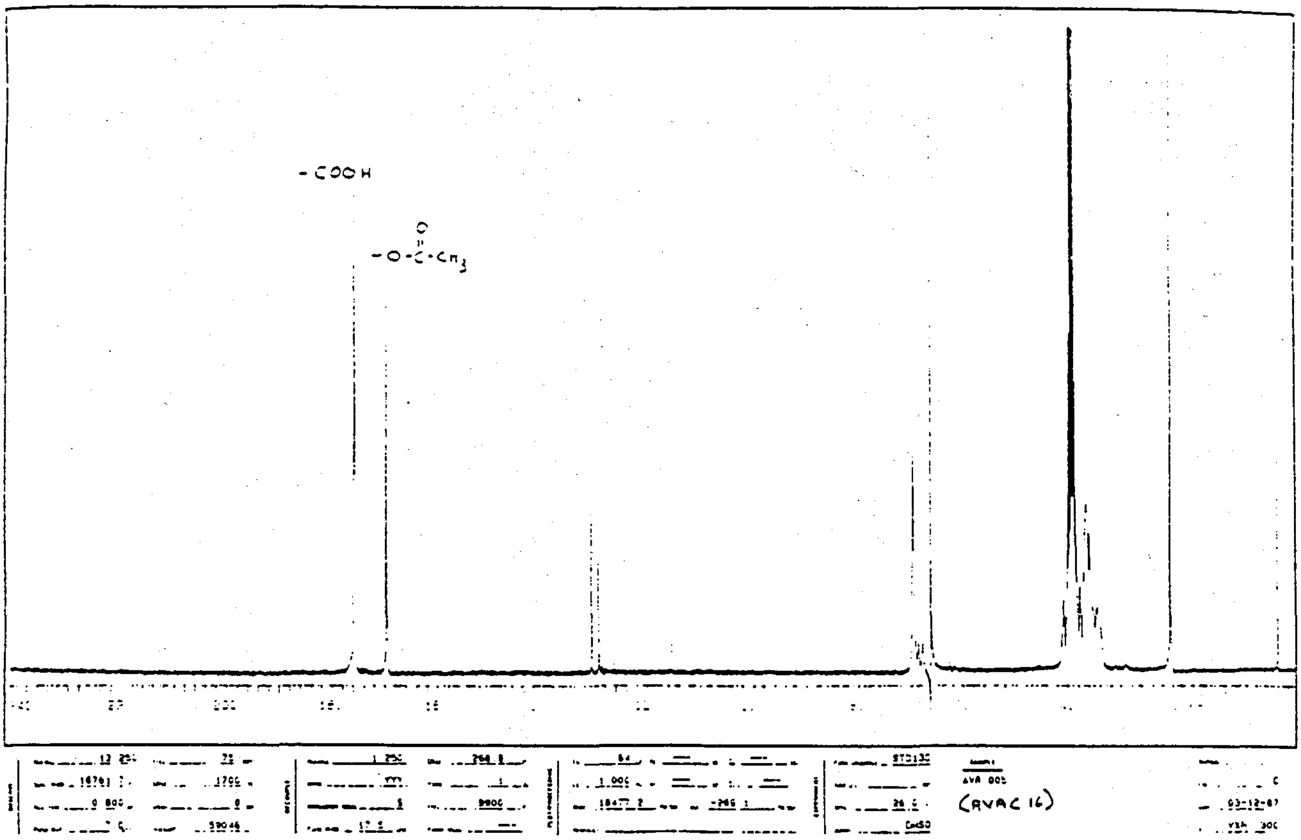


FIGURE 24:
NMR Scan of AVAC 16

TABLE 53:

Copolymer composition analysis

	Percentage of vinyl acetate in the polymer, determined by various methods		
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

The relationship between the amount of vinyl acetate in the reaction mixture and the amount in the polymer is shown in Figure 25.

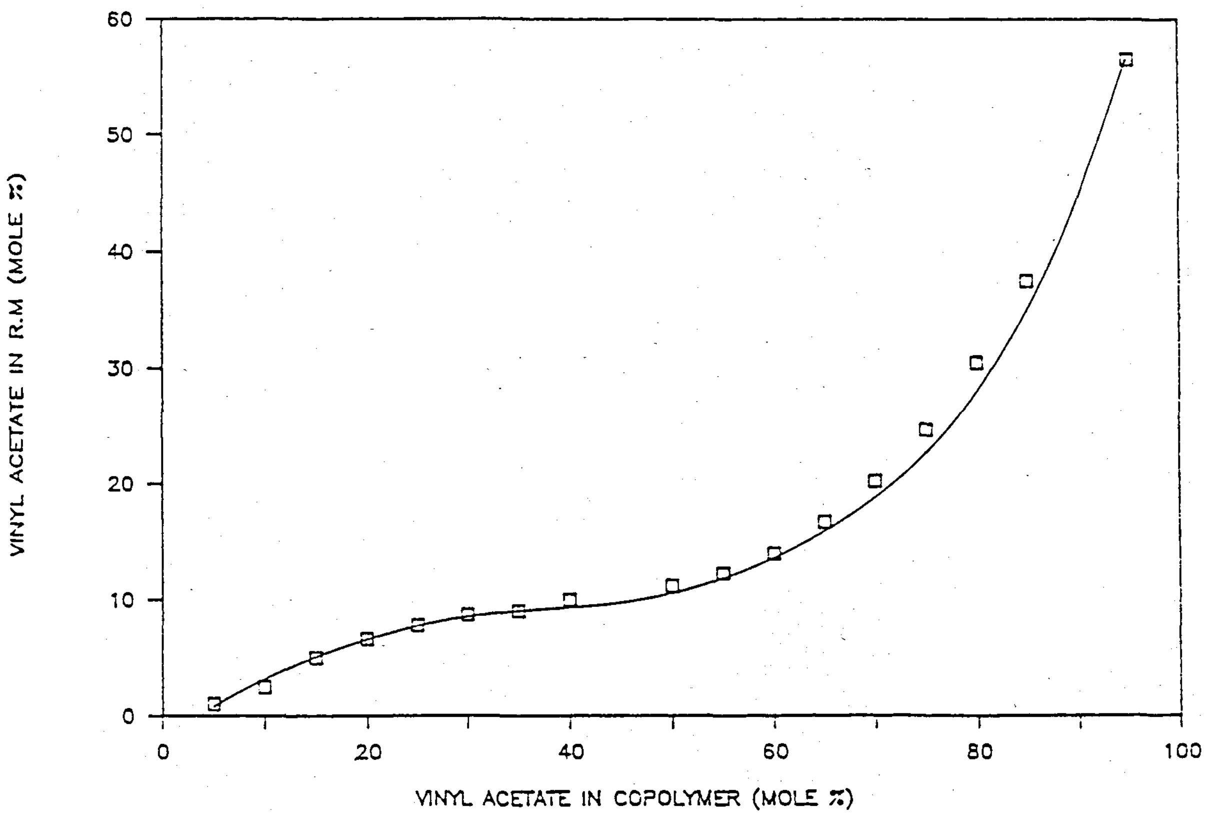


FIGURE 25:
Relationship between vinyl acetate concentration in the reaction mixture and the AVAC copolymer composition

Zirconium chelating capability. The technique used to determine this was based on the one developed by Simpson et al. **[4]**. Results are quoted in Figures 26 and 27.

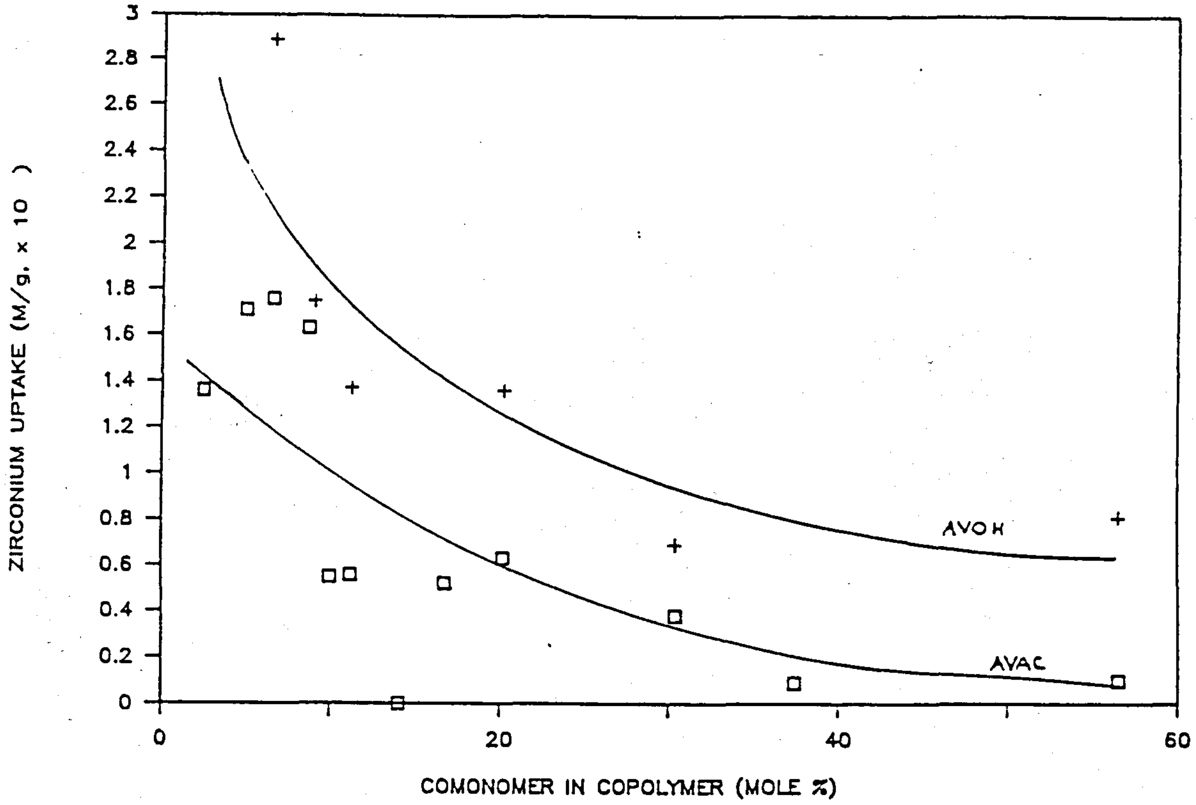


FIGURE 26:
Zirconium chelating capability of the copolymers

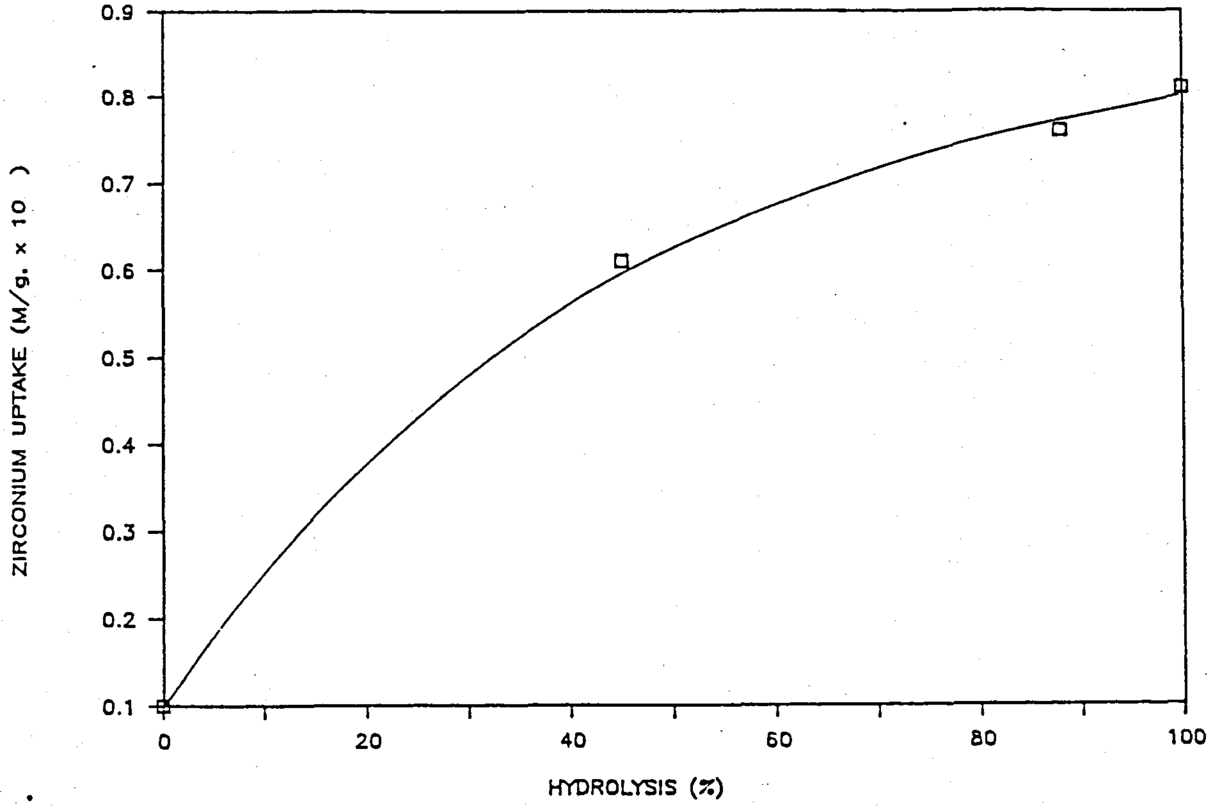
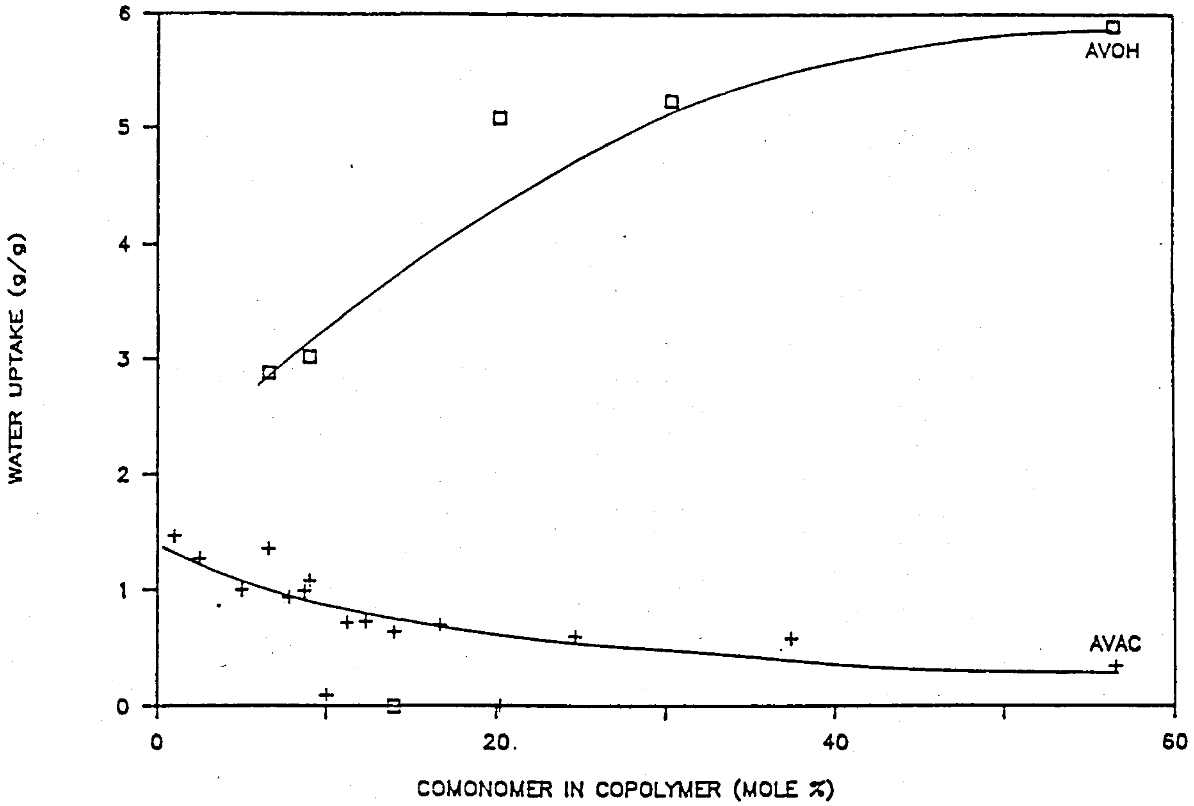


FIGURE 27:
Zirconium chelating capability as a function of the degree of hydrolysis

Figure 26 shows the decrease in zirconium uptake capability as the acrylic acid content of the copolymers decrease, and shows that the AVOH copolymers are more capable of chelating zirconium, than are the AVAC copolymers. This was to be expected, as the hydroxyl groups 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 27, which show 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 28.



<u>FIGURE 28</u>:
Water uptake capability

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 capability of the AVOH copolymers increases as the acrylic acid content decreases. The latter is due to the presence of hydrophylic (water-loving) hydroxyl groups.

6.3.2.2 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 29, and the flux results in Figure 30. In Figure 31 the relationship between water uptake capability and flux (AVAC membranes) is shown.

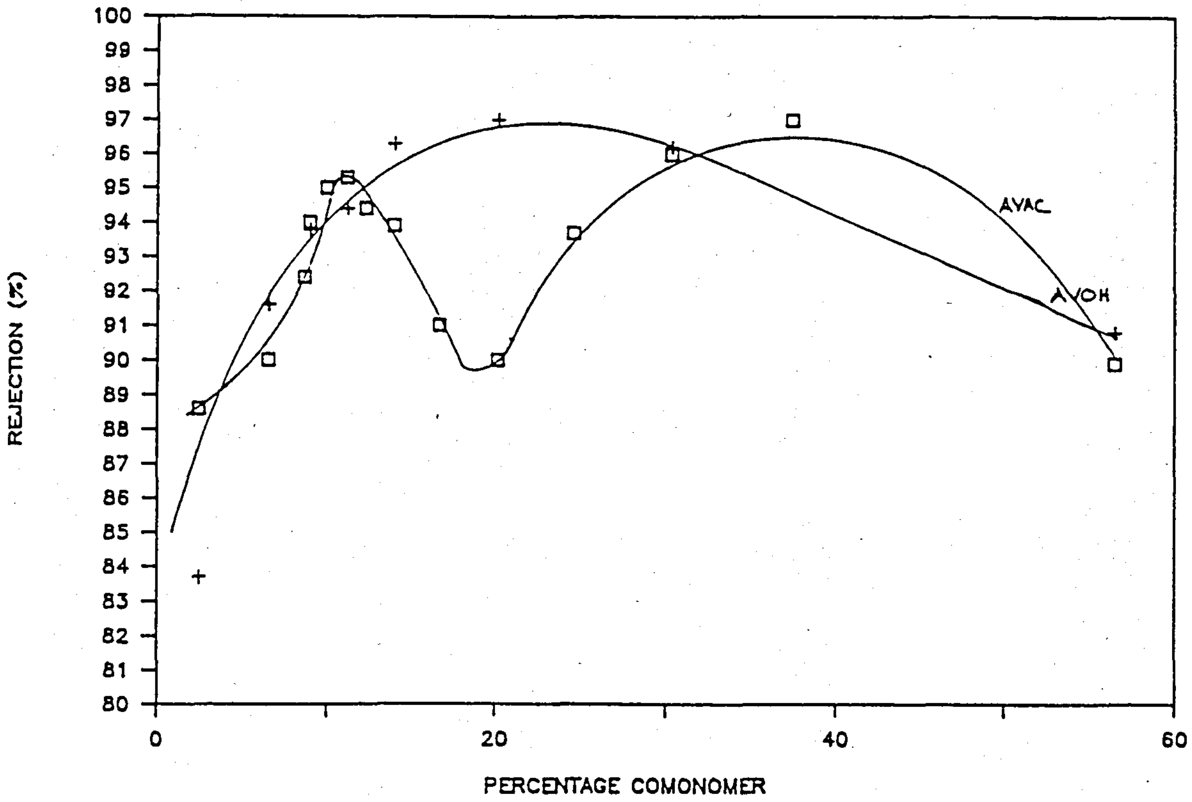


FIGURE 29:
Peak rejection figures, AVAC membranes

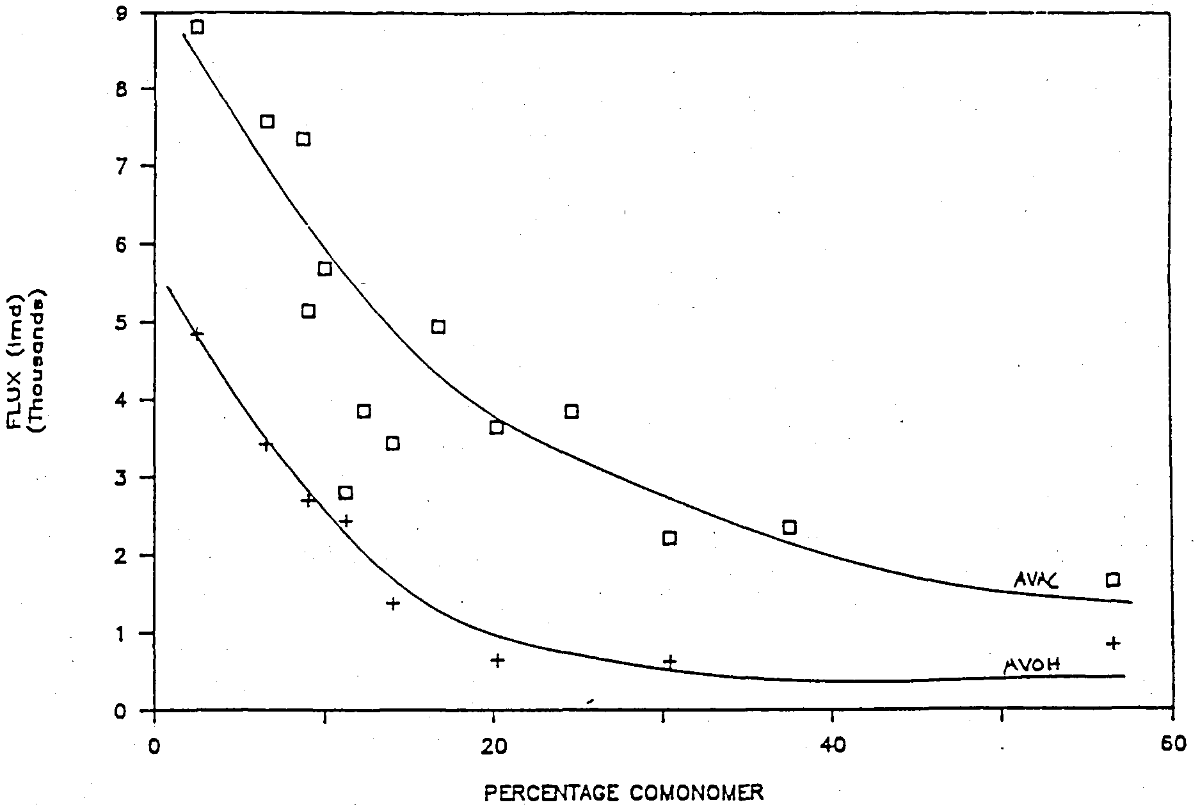


FIGURE 30:
Peak flux figures, AVAC membranes

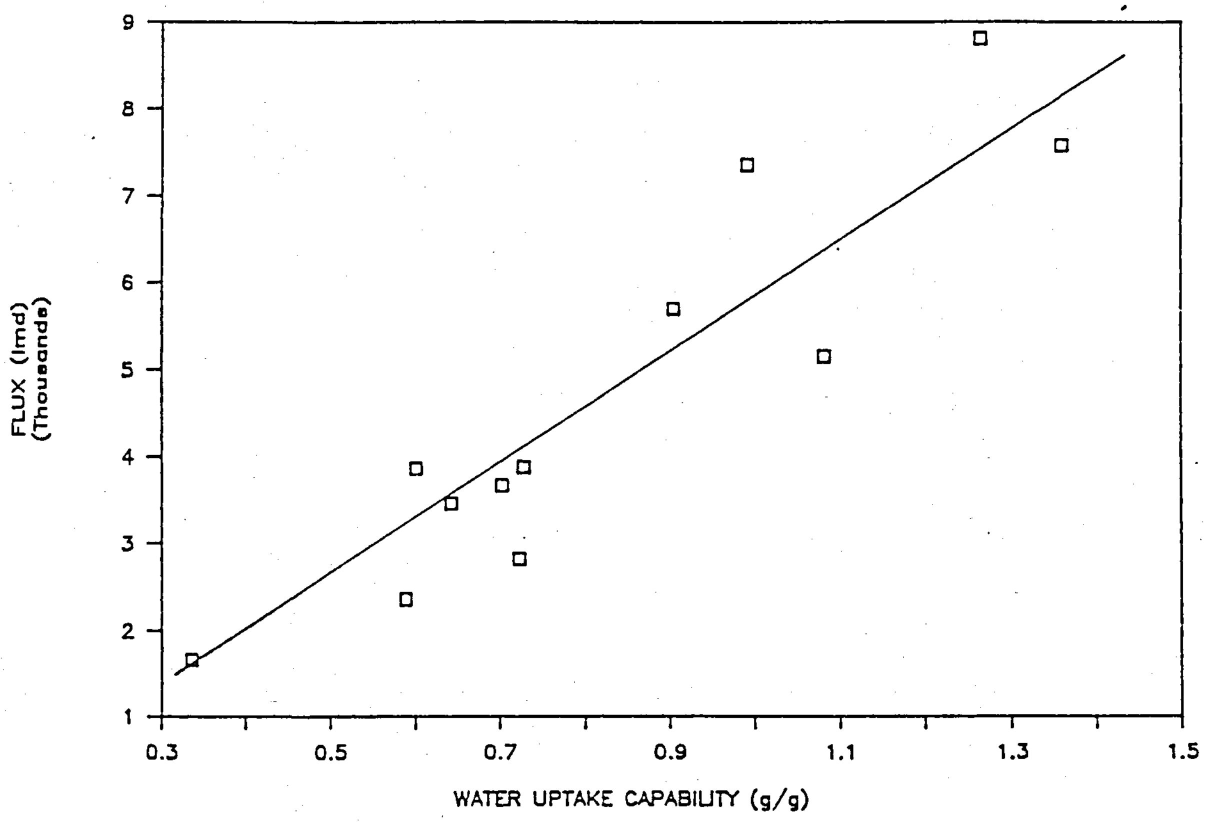


FIGURE 31:
Relationship between water uptake capability and flux, AVAC membranes

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 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 fluxes obtained at the peak rejection figures for AVAC 16 and AVOH 13 were 2,60 ml/min and 0,71 ml/min, respectively. The flux decline with changing copolymer composition is shown in Figure 30. 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 indicates 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 32.

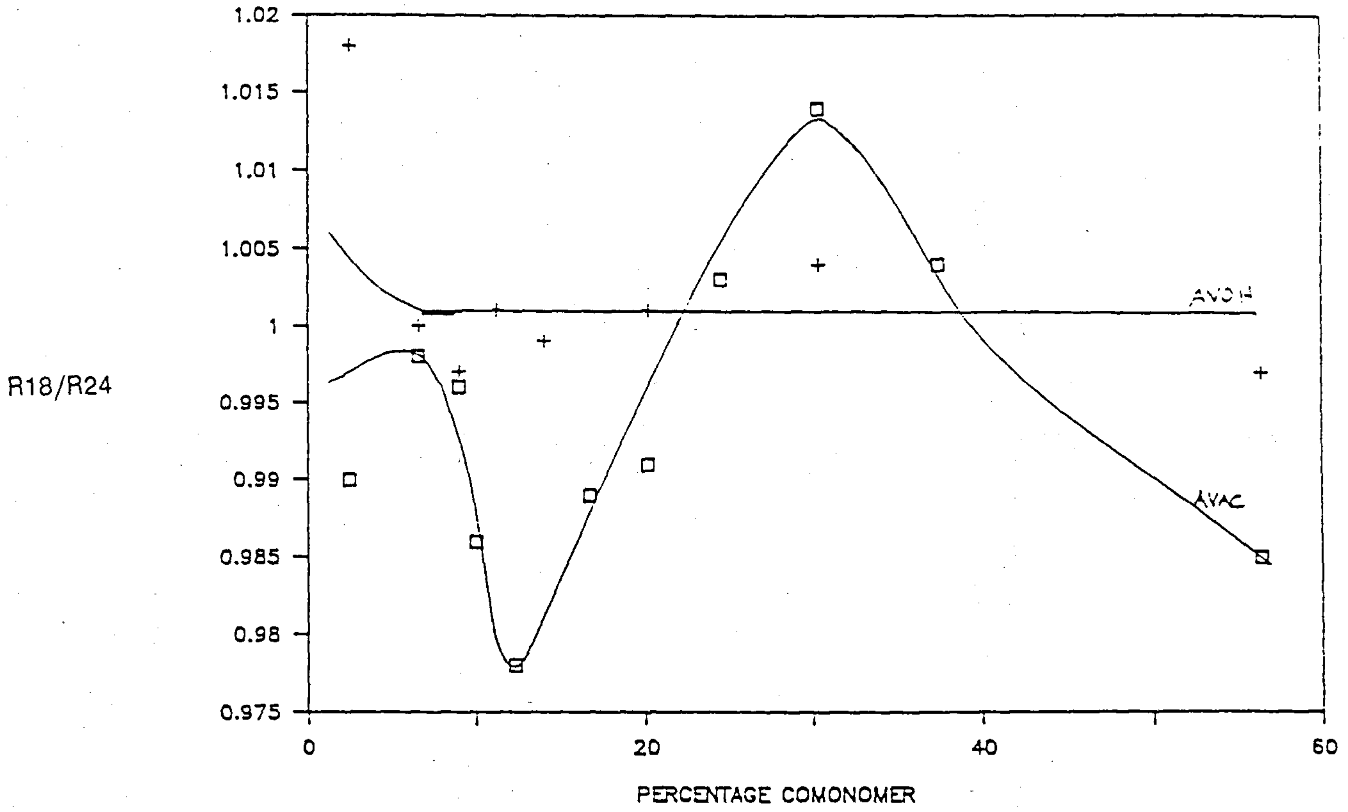


FIGURE 32:
Membrane stability, AVOH and AVAC copolymer membranes

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 26 and 27.)

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

$$R = R_i/R_7 \text{ and } J = J_i/J_7 \text{ and let}$$

$$R' = 1 - R; \quad R'' = R'/(7-i)$$

$$J' = 1 - J; \quad J'' = J'/(7-i)$$

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 33.

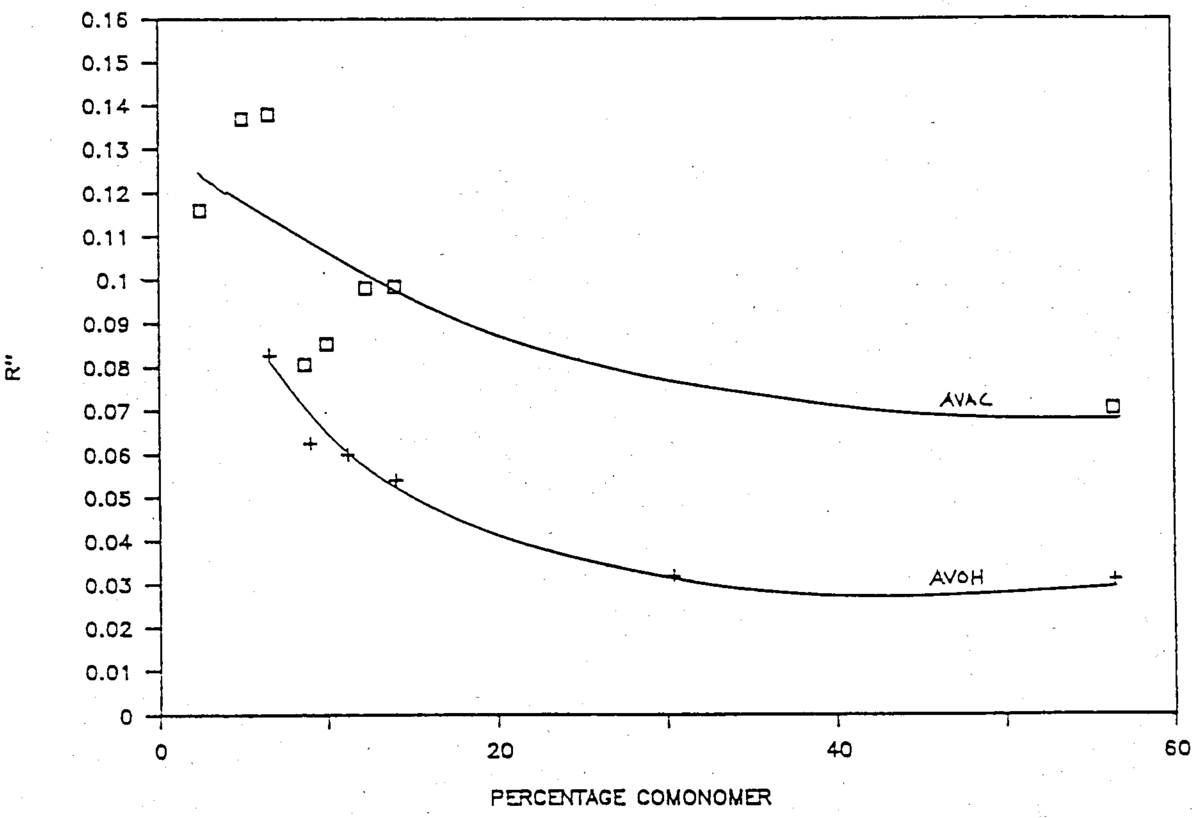


FIGURE 33:
The effect of pH

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 34.

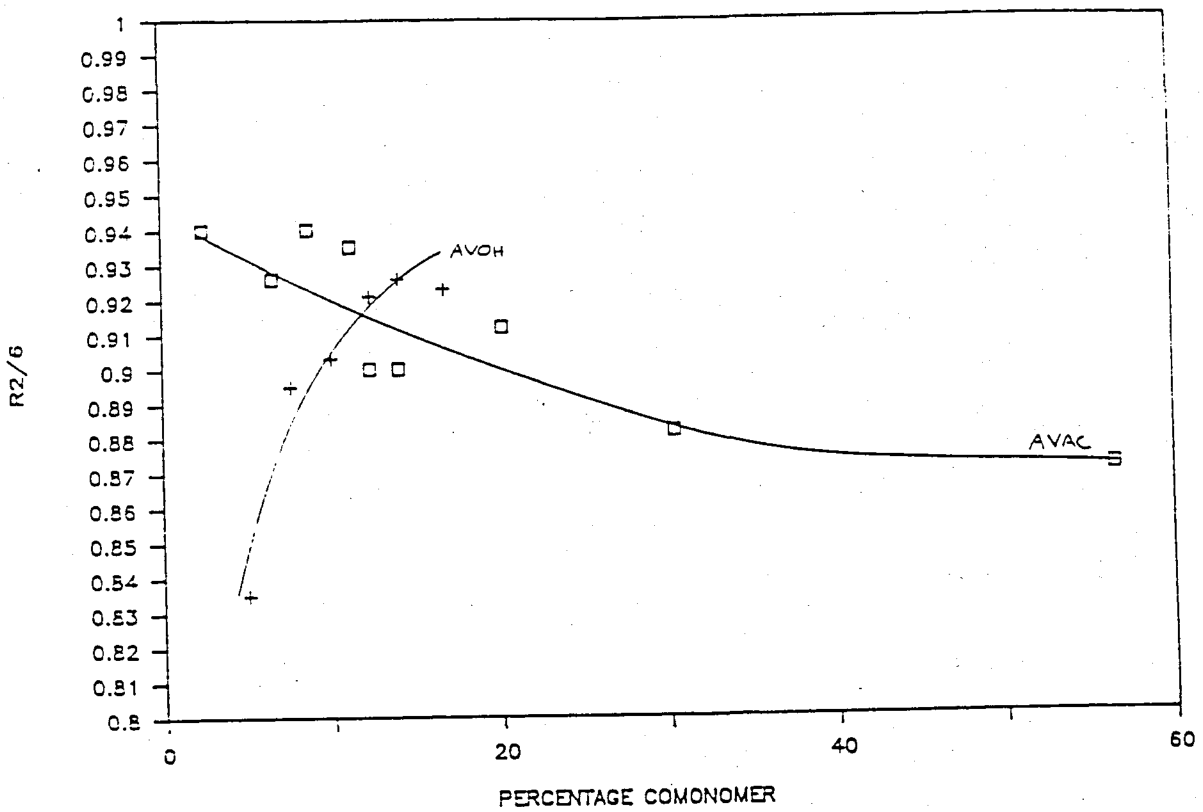


FIGURE 34:
The effect of pressure on rejection

Here it is noticeable 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 effects of copolymer composition on membrane permeability is given in Figure 35.

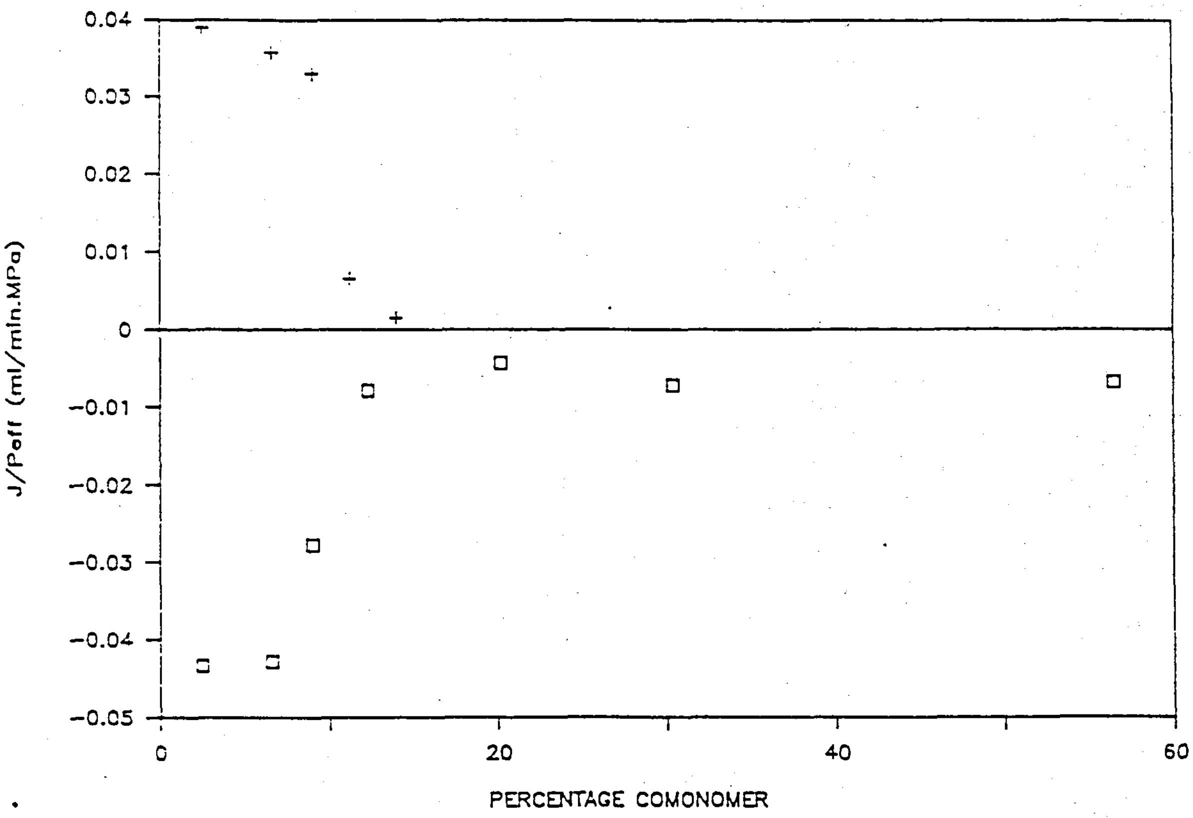


FIGURE 35:
The effect of copolymer composition on permeability

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 to 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 on the membrane. 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 36.

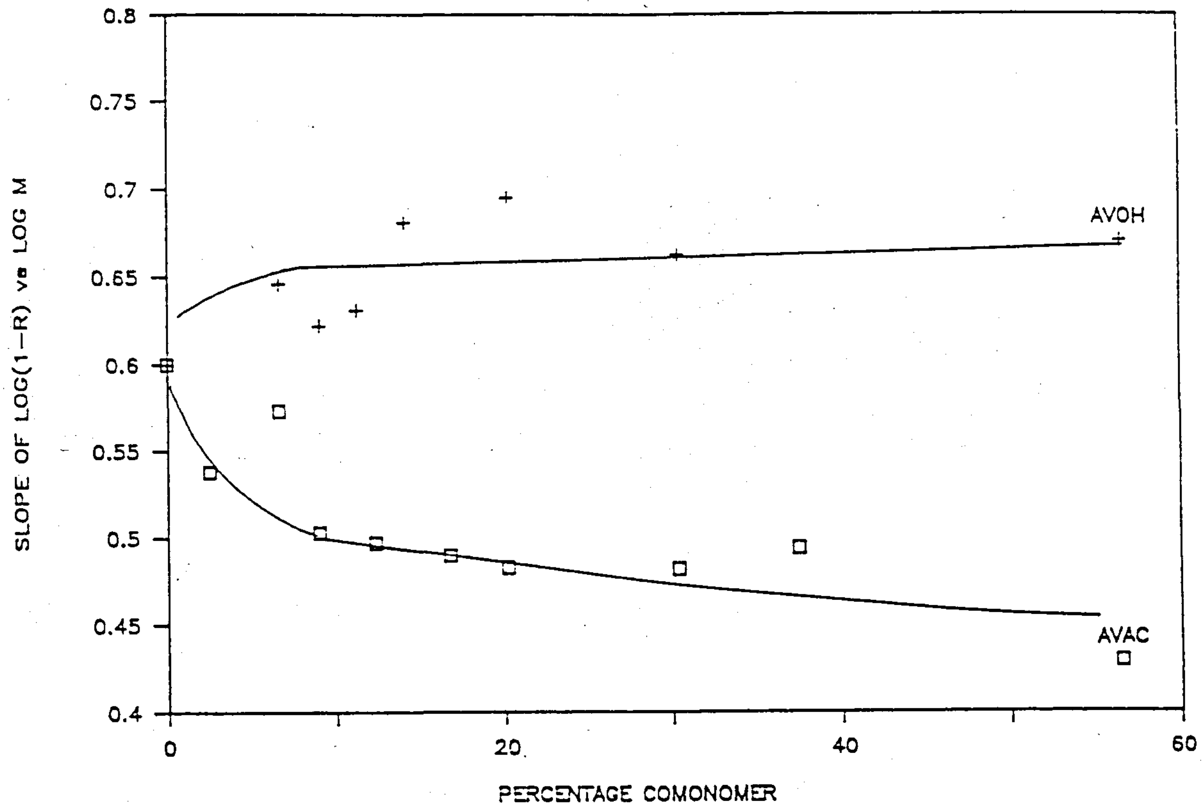


FIGURE 36:
The effect of feed concentration on rejection

These results are anomalous. The slope of the above relationship decreases for an increasing comonomer content in the AVAC copolymer membranes, as was 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 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 to 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 37.

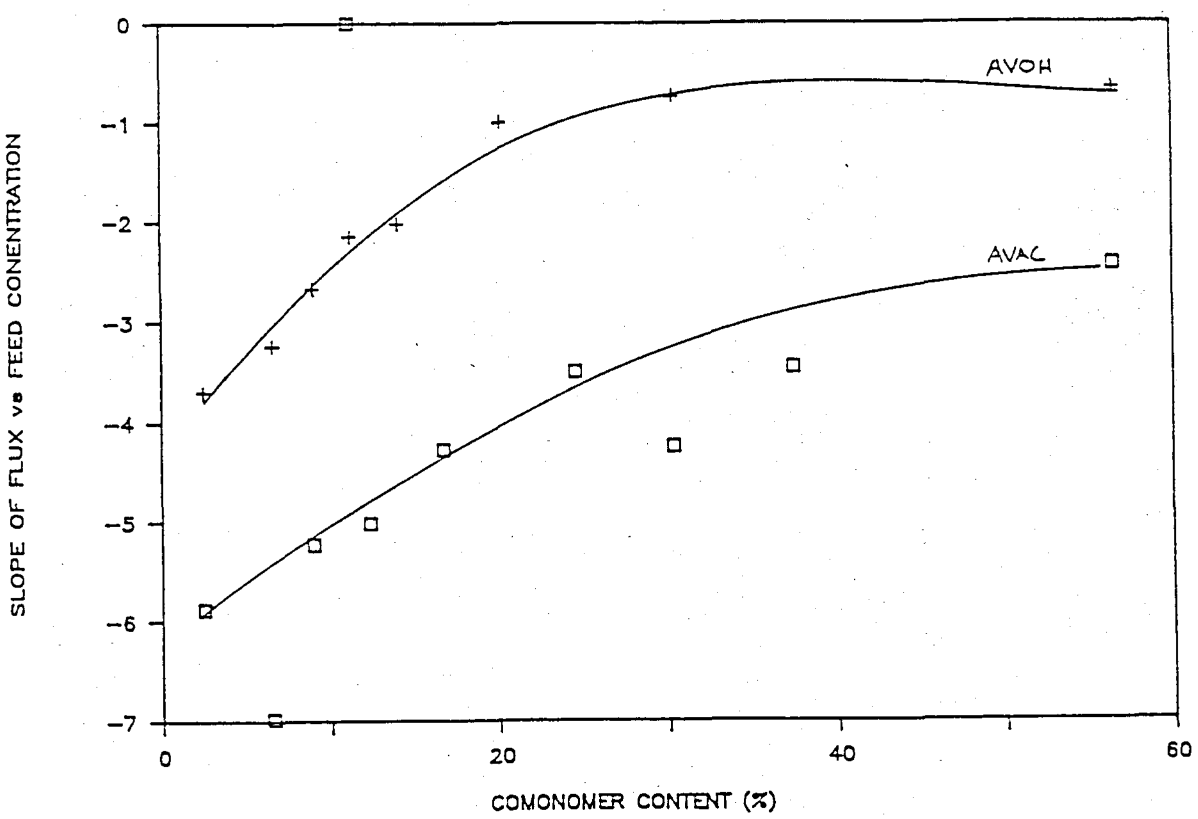


FIGURE 37:
The effect of feed concentration on flux

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.

6.3.2.3 Developments and discoveries arising from 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 lmd; this relates to a flux of about 1,70 - 2,20 ml/min, using our test facilities. From the preceding sections it is obvious that many of the membranes formed by IPS were superior in their rejection and flux capabilities to that of membranes made from 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 54.

TABLE 54:

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 (lmh)		
	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 code-named 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 55 and 56.

TABLE 55:
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 56:
The effect of time on the flux behaviour of dynamically formed hydrous zirconium oxide-AVOH 86/2 membranes

Time (h)	Flux (lmh)		
	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 Tables 55 and 56 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 the tables. 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, compared with 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 polymer AVOH 86/2 approached, in broad terms, that of AVOH 11, and the slopes 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, Transvaal, S.A. 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 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 contain 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 57.

TABLE 57:

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

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 57 indicate very good rejection of a broad spectrum of widely differing constituents. Notable here are substances such as the thiocyanates, acids and hydantoins. Based on these results 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, and the material most commonly used is porous stainless steel. In the laboratory, the support used was Millipore ultrafilters (HA rated 0,45 μm). Porous stainless steel tubes are very expensive. It was decided, at the first attempt, to try to form dynamic membranes in the equipment normally used, and at the operating conditions normally used, on a variety of ultrafiltration membranes comprising poly(ether sulfone) microfibres on a polyester backing. Four samples of these materials were obtained from Carl Freudenberg (R), tradename VILEDON. The results of dynamic membranes formed on these supports are given in Table 58. The polyelectrolyte used was the commercially available Acrysol A3.

TABLE 58:

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

2. Support pore size : 15 µm (maximum)

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

3. Pore support size : 150 µm (maximum) (4 MPa)

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

4. Pore support size : 188 µm (maximum)

Rejection (%)			Flux (lmh)		
1	2	3	1	2	3
	48,4 (85,5) [85,5]	44,4 (84,2) [84,0]		498 (193) [196]	506 (189) [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 54). 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 tube was used as the support.

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 made in-house at IPS.

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 59. The measurements of the individual cells were always close to that of the average.

TABLE 59:

The flux and rejection of hydrous zirconium oxide dynamic membranes, formed on an IPS tubular UF support

Run time (h)	Rejection (%)	Flux (lmh)
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 time, the flux decreased from 5 400 lmd to 1 480, 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 lmd to 728 lmd, 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 development 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 pressure. 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 60.

TABLE 60:
The performance of dual layer dynamically formed membranes on tubular UF support materials

Polyelectrolyte	Pressure (MPa)	Flow rate (l/h)	Rejection (%)	Flux (lmh)
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 59), 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 those 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 61.

TABLE 61:
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 (lmh)
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. Refining the technique and using other polyelectrolytes led to even better results. These are given in Table 62.

TABLE 62:
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 gave encouraging results. Results are given in Table 63.

TABLE 63:
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

6.3.2.4 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 received to date. Four polymers were sent to the University of Natal for evaluation. Two polymers were evaluated, and the results of which are given in Table 64.

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

TABLE 64:

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)
08/11/88	Zr*	6000	4,3	588	39	2,46
09/11/88	Zr-PAA*	6000	4,3	195	80	2,30
09/11/88	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.

6.3.3 CONCLUSIONS AND RECOMMENDATIONS

During this programme, a number of acrylic acid copolymers were synthesized and, when tested as dynamic membranes; they gave better salt rejection than did the poly(acrylic acid) membranes tested under identical laboratory conditions. The use of cheap plastic ultrafilters (poly(ether sulfone) on polyester fabric) as dynamic membrane subtrates has been sucessfully demonstrated. The use of dynamic membrane chemistry, developed during this research, to make low-rejection, low pressure membranes has been demonstrated; it remains, however, an area that needs to be investigated more fully. The research has led to a better understanding of the way in which dynamic membranes function. 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.

6.3.3.1 General

(i) The peak rejection figures obtained were similar for the homogeneous AVAC and AVOH copolymers membranes, averaging 97,0%. These results are much superior to those obtained with the state-of-the-art poly(2-propenoic acid);

(ii) The results obtained with non-homogeneous AVOH-86/2 membranes were exceptional, giving 99% rejection and fluxes as good as the state-of-the-art poly(2-propenoic acid);

(iii) The fluxes of the AVOH copolymer membranes are always lower than the corresponding ethenyl acetate copolymer membranes;

(iv) The AVOH copolymer membranes are, in general, more stable than the AVAC copolymer membranes. This enhanced stability is due to the presence of the alcohol groups;

(v) The rejection and flux behaviour in terms of copolymer composition with a change in pH is similar for the AVAC and AVOH membranes;

(vi) The rejection behaviour in terms of copolymer composition with a change in pressure is different for the AVAC and AVOH membranes, although the reason for their respective behaviour is the same. The rejection behaviour with changing feed concentration for the AVAC and AVOH copolymer membranes is anomalous;

(vii) The AVOH copolymer membranes are all more sensitive to feed concentration than the corresponding AVAC copolymer membranes;

(viii) The flux change of both the AVAC and AVOH copolymer membranes in terms of copolymer composition, with changing feed concentration is more severe as the 2-propenoic acid content of the membranes increase.

6.3.3.2 Developments and discoveries resulting from, and pendant to, the study

(i) The AVOH 86/2 membranes are a viable proposition for the treatment of industrial wastes;

(ii) There is a definite possibility that supported poly(sulphone) or poly(ether sulphone) ultrafiltration membranes could be used as dynamic membrane support materials.

6.3.3.3 Suggested future research

(i) Optimization of membrane formation conditions of several of the AVAC and AVOH copolymer membranes must be undertaken.

(ii) The use of poly(sulphone) or poly(ether sulphone) as support materials for dynamic membranes should be investigated, in conjunction with low pressure membrane formation experiments;

(iii) The rejection capabilities of divalent salts and organic solutes hsould be investigated with some of the better AVOH and AVAC copolymer membranes;

(iv) Various novel co- and terpolymer structures can be envisaged which might give comparable or even improved membrane performances;

(v) The anomalous behaviour of the AVOH membranes with feed concentration variations should be investigated;

(vi) The effect of ageing the zirconium membranes prior to polyelectrolyte deposition should be investigated;

(vii) The use of mixed hydrous metal oxides for the base membrane could be studied.

6.4 THE PERIOD JANUARY 1989 TO DECEMBER 1990

6.4.1 BACKGROUND

In this period, Gerber **[5]** concentrated on the synthesis of poly(acrylic acid-co-hydroxyethyl acrylate) (HEA) and poly(acrylic acid-co-hydroxyethyl methacrylate) (HEMA). These polyelectrolytes were then evaluated as dynamic membrane polymers. Both the above polyelectrolytes are crosslinkable, and it was envisaged that the stability of dynamic membranes could be improved by crosslinking them *in situ*, thereby rendering them less susceptible to changes in pH and feed, concentration, a common drawback with charged membranes.

6.4.2 POLYMER SYNTHESIS AND CHARACTERIZATION

A method of copolymerizing acrylic acid with hydroxyethyl acrylate and hydroxyethyl methacrylate was established. The methods are fully explained in the M.Sc.-thesis of Gerber **[5]**. The series of polymers were analyzed by means of ^{13}C NMR spectroscopy. The synthesized polymers were characterized in terms of their composition and molecular mass with ^{13}C NMR and solution viscometry respectively. In the water uptake experiment it was established that an increase in the HEA and HEMA content in the polyelectrolyte led to an increased amount of water being absorbed. This was attributed to the structure and chemical composition of the propenoate monomers. In the zirconium uptake experiment it was determined that the presence of the HEA and HEMA moieties in the copolymers led to increased zirconium chelating ability. Due to the flexibility and length of the alcohol-containing acrylate chain, chelation through both alcohol and acid groups seemed to be less sterically hindered and energetically preferred when compared with chelation through only acid groups. It was further established that a certain minimum number of acid groups were necessary for good chelation.

Copolymer compositions are given in Table 65 below.

TABLE 65:

Composition of the HEA and HEMA copolymers

Polymer	AA (%)	HEA (%)	HEMA (%)
HEMA 1	21,0		79,0
HEMA 2	48,0		52,0
HEMA 3	71,0		29,0
HEA 1	24,0	76,0	
HEA 2	50,0	50,0	
HEA 3	73,0	27,0	

An indication of the polymer molecular masses were obtained by means of dilute solution viscometry. Results are given in Table 66, together with the water uptake and zirconium chelating data.

TABLE 66:

Intrinsic viscosity, water uptake capability and zirconium chelating capability of HEA and HEMA copolymers

Polymer	Viscosity capability (g H_2O/g Polymer)	Water uptake capability (Zr g x10^{-3}/g polymer)	Zr Chelating
HEMA 1	0,518	1,533	23,71
HEMA 2			
HEMA 3	0,757	1,085	36,89
HEA 1	0,062	1,453	14,82
HEA 2	0,106	1,185	28,20
HEA 3	0,104	1,022	33,21

It is noticed from Table 66 that the hydrodynamic size of the HEA copolymer range is far smaller than that of the HEMA copolymers, probably due to the absence of the methyl group in the a position of the comonomer. Interestingly, the water uptake decreases as the acrylic acid content increases. Similarly, the Zr uptake capability increases as the acrylic content of the copolymers increase. This was to be expected.

6.4.3 MEMBRANE PERFORMANCE

6.4.3.1 Mechanism of rejection and flux

Membrane rejection was due to a combination of two processes:

- Donnan exclusion due to the presence of ionized carboxylic acid groups;

- Rejection due to the presence of the neutral hydroxy monomers which is based on frictional forces exerted on the permeating water and water-coupled salt ions.

It was established that a minimum charge density was necessary to obtain an appreciable amount of rejection (more than 50% 2-propenoic acid), but that the presence of the hydroxy monomers did enhance rejection.

Membrane flux was governed by the friction exerted on the permeating water by bound water and water-coupled salt ions.

The increased friction exerted on permeating water due to the increased fluid holding-capacity of the HEA and HEMA copolymers, when compared to poly(2-propenoic acid), was borne out in the reduced flux of these membranes.

6.4.3.2 Peak rejection and flux

The peak rejection and flux figures obtained with these copolymer membranes are shown in Figures 38 to 41.

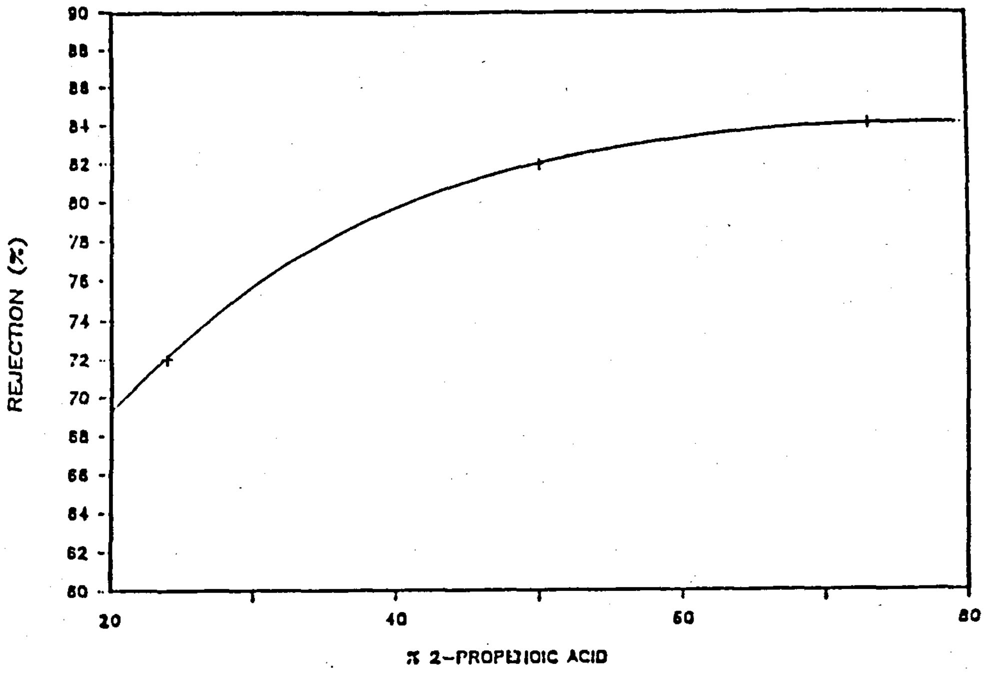


FIGURE 38:
Membrane peak rejection HEA copolymers

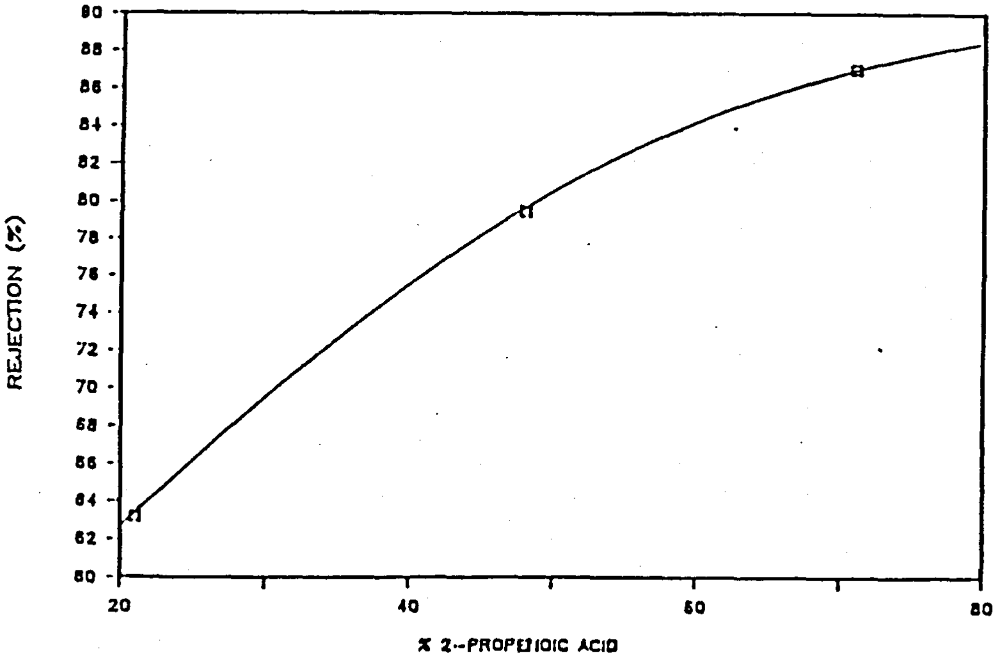


FIGURE 39:
Membrane peak rejection HEMA copolymers

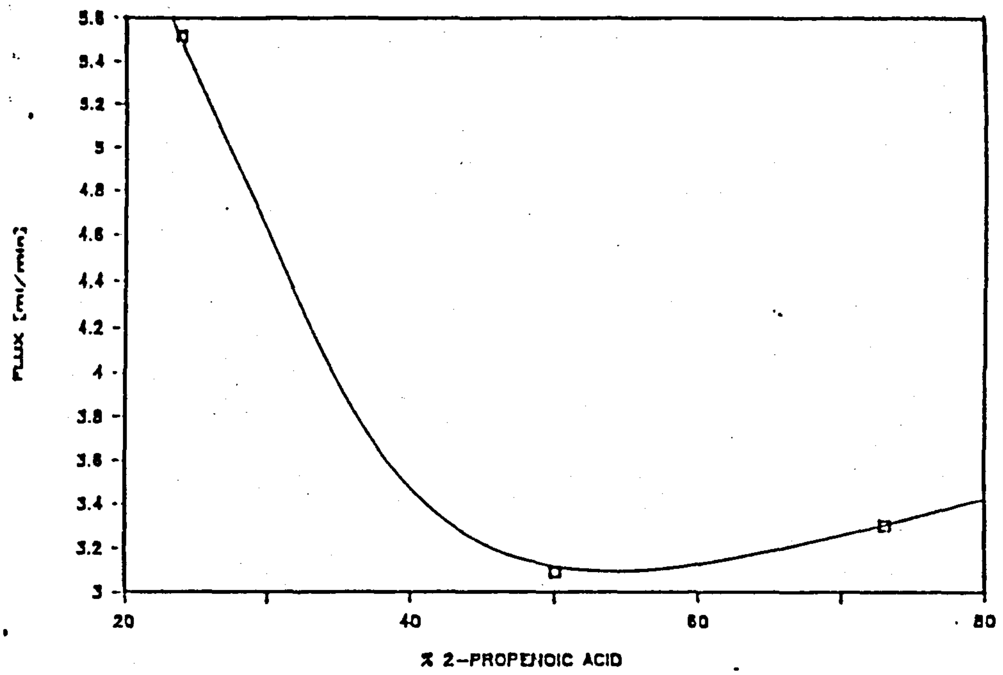


FIGURE 40:
Membrane peak flux HEA copolymers

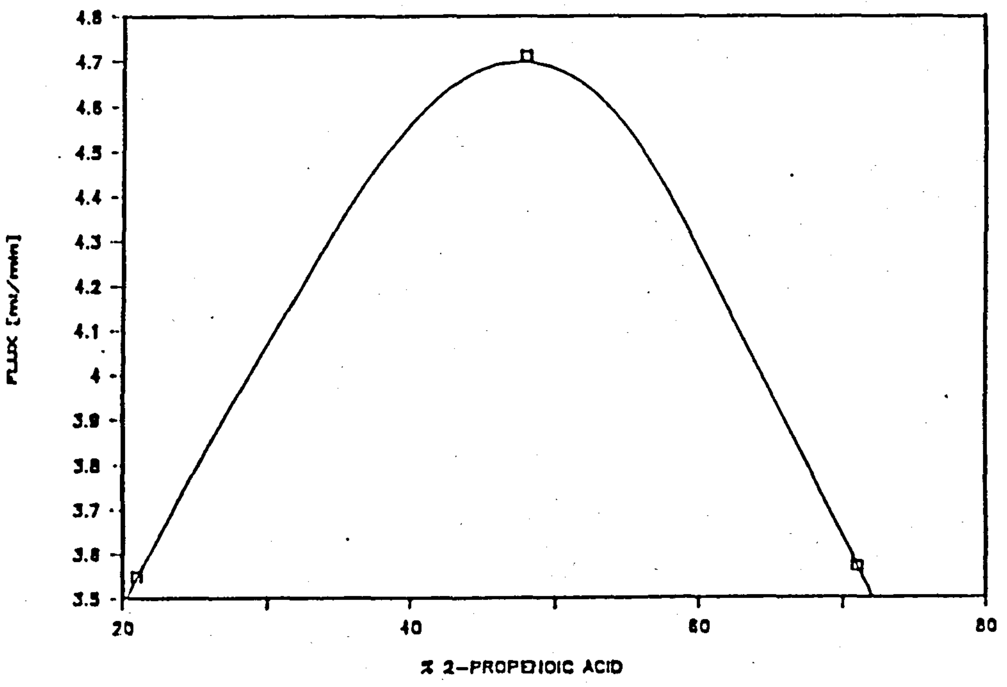


FIGURE 41:
Membrane peak flux HEMA copolymers

Membranes were evaluated in terms of their sensitivity to pH and salt concentration and then crosslinked in situ. Evaluation in terms of pH and feed salt concentration sensitivity was then repeated. The sensitivity to pH change was determined by the value R" (see Section 6.3.2.2) and the senstivity to feed salt concentration by the slope of the log(feed salt concentration) (log (M)) vs log(1-observed rejection) (log(1-R_{obs}) plots. These results are shown in Table 67.

TABLE 67:
The effect of crosslinking on HEA and HEMA dynamic membranes

Membrane Polymer	R"	Rc"	S	Sc
HEMA 1	0,149	0,121	0,101	0,115
HEMA 2	0,105	0,096	0,403	0,395
HEMA 3	0,056	0,060	0,447	0,383
HEA 1	0,152	0,137	0,368	0,271
HEA 2	0,078	0,085	0,476	0,343
HEA 3	0,064	0,047	0,354	0,355

From Table 67 it can be seen that the crosslinking that can be effected has some effect on the pH and feed salt concentration of the above membranes.

Peak rejection values were obtained at 71% 2-propenoic acid and 73% 2-propenoic acid for the HEMA and HEA copolymers respectively. This indicated that Donnan exclusion should be the dominant mechanism of rejection and that the incorporation of the neutral HEA and HEMA monomers increased rejection.

No relationship could be established between the variation in copolymer composition and membrane flux, but the fluxes for the copolymers were substantially lower than that poly(2-propenoic acid) due to the increased amount of friction exerted on the permeating water by bound water.

6.4.3.3 The effect of pH

All the membranes showed an increase in rejection when the pH was raised. This was due to an increased amount of carboxylic acid groups ionizing when the pH was raised. This will in turn increase the rejection due to Donnan exclusion. No hydrolysis occurred in any of the membranes when the pH was raised above 7,0 which indicated good chelation of the polyelectrolyte to the zirconium oxide base membranes.

Membrane flux showed a decline when the pH was raised. This was due to an increased amount of bound water in the polyelectrolyte causing increased friction being exerted on the permeating water.

The pH dependence of rejection as a function of the copolymer composition showed a decrease with increase in acid content while flux showed an increased dependance on pH with increasing acid content.

6.4.3.4 The effect of feed salt concentration

Increase in the HEA and HEMA monomer content in the copolymers led to the membrane charge density being reduced. This reduced the dependence of rejection on feed salt concentration.

Increased neutral monomer content in the copolymers also reduced the dependence of membrane flux on feed salt concentration.

6.4.3.5 The influence of crosslinking

Crosslinking reduced the amount of free carboxylic acid and hydroxyl groups. This reduced the membrane charge density and hydrophilicity.

The dependence of rejection on pH was reduced by crosslinking, while the membranes showed lower fluxes over the whole pH range after crosslinking.

The reduced membrane charge density reduced the influence of feed salt concentration on rejection.

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   (Appendix 3A, first draft - final report.)

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   (Appendix 3B, first draft - final report.)

6.6 PUBLICATIONS ARISING FROM THE RESEARCH

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2. "Copolymers for dynamically formed hydrous zirconium (IV) oxide polyelectrolyte membranes with enhanced flux and rejection properties". A.J. van Reenen and R.D. Sanderson in "Advances in Reverse Osmosis and Ultrafiltration" T. Matsuura and S. Sourirajan Ed., pp 587 - 598. Published by NRCC, 1989.

3. "Dynamically formed hydrous zirconium (IV) oxide-polyelectrolyte membranes. III. Poly(acrylic acid) and substituted poly(acrylic acid) homo, co and terpolymer membranes" by A.J. van Reenen and R.D. Sanderson, *Water SA*, 15(4) (1989), 247 - 252.

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(i) "Synthetic materials as substrates for dynamically formed membranes", A.J. van Reenen and E.P. Jacobs.

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

SECTION 4

7. DEVELOPMENT OF A LOW-COST HIGH-PRESSURE DYNAMIC MEMBRANE MODULE

7.1 BACKGROUND

The proposed programme in this area of the work reads as follows:

(i) Engineer a nonwoven-fabric-supported microporous PES substrate membrane.
(ii) Develop a parallel-flow membrane pressure support system (ring support concept) and module. Specifications: 6 MPa, 90°C and low permeate-side pressure drop.
(iii) Initiate study with thermoset support rings.
(iv) Evaluate prototype ring and module designs at the pressure and temperatures specified and at high concentration levels of oxidative chemicals, alkali, acid and surfactant.
(v) Finalize ring design.
(vi) Study epoxy systems as an alternate support-ring material and as a potting material.
(vii) Evaluate module housing material and relative cost: GRP, epoxy- coated ferrous and non-ferrous shrouds.
(viii) Evaluate dynamic membrane module and support-membrane system in simulated studies with real effluents.

Research conducted under this heading was aimed at solving some of the problems associated with the scale-up operation in the implementation of bench-scale research findings. The initial findings resulting from dynamic membrane formation and development work, conducted in small radial flow, and channel flow, flat-cell devices led to this work being attempted.

Of the above, the following have to be considered as the two most important aspects of this programme:

(i) Develop processes and procedures to ensure reproducible fabrication of tubular substrate membranes which can withstand the adverse conditions which exist when dynamic UTF membranes are formed or stripped. Also, develop techniques to ensure consistent performance from dynamic membranes deposited on synthetic substrate membranes.
(ii) Develop a membrane element and module best suited for the conditions of membrane formation and operation.

Much of the success of this programme depended on the favourable outcome of the work encompassed in (i) above.

7.2 SUBSTRATE MATERIALS DEVELOPMENT

7.2.1 BACKGROUND

Traditionally, porous ceramic and stainless steel tubes have been used as substrates for dynamic UTF membranes. However, the great cost of these materials affects the commercial acceptance of such a membrane system, disregarding the relatively low intrinsic salt-rejection of the traditional Oak Ridge, (O RNL; U.S.A.) membrane of ~93%. The cost of the membrane module can be reduced considerably if porous stainless steel substrates can be replaced by synthetic microporous membranes.

In this regard the use of high-Tg thermoplastic polymers for use as substrate-membrane forming materials was to be investigated.

However, the following had to be established first:

(i) Establish the effectiveness of microporous tubular PES membranes as substrates for zirconium base-membranes and polyelectrolyte dynamic membranes at formation pressure conditions ranging from 2-4MPa and cross-flow velocities ranging from 1-6m/s.
(ii) Determine to what extent repeated re-use of a synthetic substrate membrane affects the performance of dynamic membranes.
(iii) Establish whether asymmetric substrate membrane formation conditions (i.e. factors which control membrane morphology) affect the performance of both the inorganic zirconium base-membrane and dynamic UTF membrane.

A range of tubular polyethersulphone (PES) UF membranes were evaluated for their suitability to act as substrates for dynamic membranes. Fixed conditions of formation were used to form both the hydrous Zirconium IV oxide base and dual-layer polyelectrolyte membrane.

7.2.2. EXPERIMENTAL

Various tubular PES UF membranes were produced by the wet phase-inversion method by techniques described elsewhere. These membranes were evaluated for their suitability as alternative substrates for dynamic membranes by a membrane formation technique fairly similar to that originally proposed by ORNL.

7.2.2.1 Evaluation and experimental procedures

All membranes were evaluated (200kPa, 20°C, 1m/s) for their initial permeability to pure RO tap water before being used for dynamic membrane formation. The membranes were also evaluated (500kPa, 20°C, 1m/s) for their UF performance against an 0,5% m/m feed solution of Kollidon 30 (polyvinyl pyrrolidone, BASF). Kollidon 30 has a molecular mass of 45 000 dalton. (See Table 68 for a list of membrane UF performances).

TABLE 68:
Pure water flux and UF performances of PES substrate membranes

Membrane code	Pure Water Flux* [lmd]	UF flux** [lmd]	UF retention** [%]
528/723	670	1 000	83,3
521/342/10	16 953	1 100	75,8
527/333	6 500	1 200	69,7
523/341	7 400	1 300	68,4
519/719	11 200	1 200	67,9
520/337	21 300	1 300	62,4
521/342/20	22 700	1 500	61,8
524/341	8 700	1 200	61,5

* 200 kPa, 20°C, 1 m/s;

** 500 kPa, 20°C, 1 m/s, 0,5% m/m Kollidon 30 (PVP, mol mass 45 000 dalton).

As part of the evaluation procedure followed to determine the suitability of the various synthetic membrane substrates to support dynamic membranes, hydrous Zr(IV)-oxide membranes were first formed and stripped repeatedly from the various UF substrates. Second, a final hydrous Zr(IV)-oxide coating was deposited as a base-layer for subsequent treatment with a polyelectrolyte to finally form the required dual-layer dynamic membrane.

7.2.2.2 Formation of the hydrous zirconium (IV) oxide matrix

The method for the formation on the hydrous zirconium oxide matrix involved the addition of 1,3 g $Zr(NO_3)_4$ to the 30ℓ feed tank of the RO test loop, already containing 2g/ℓ $NaNO_3$ at a pH of 3,6. The feed solution was circulated across 4x1m and 1x400mm series connected 13mm ID tubular membranes, at an initial linear cross-flow velocity of 0,9m/s and a feed pressure of 500kPa. The cross-flow velocity and feed pressure were increased at regular 3min. intervals in steps of 0,3m/s and 500kPa to final membrane formation values of 2,6m/s and 3MPa. The pH and temperature of the feed solution were maintained at 3,6 and 35°C respectively from the start of the formation cycle. A total of 60 min. was allowed for the formation of the Zr-oxide base-membrane, before the membranes were evaluated for salt retention and water flux. The Zr base-membrane was then either stripped during a pH 1 wash cycle of one hour, or a polyelectrolyte layer was deposited on the base-layer.

7.2.2.3 Polyelectrolyte deposition

After deposition of the base-layer, the pH was lowered to 2 with HNO_3, and the test loop was repeatedly rinsed with pure water (also adjusted to pH 2) to remove unspent zirconium from the system. The $NaNO_3$ concentration of the feed solution was readjusted to 2g/ℓ; Polyacrylic acid (50 mg/ℓ) (Acrysol A3, Supacryl equivalent) was then added to the feed solution. The feed temperature, linear velocity and pressure were maintained at 35°C, 2,6m/s and 3MPa, respectively, throughout this and the next treatment.

The pH of the feed solution was slowly adjusted upwards every 30min. in 0,5 increments from the starting value of 2 until pH 5 was reached. From then on it was increased by 1 pH unit to the end-value of 7. After allowing the system to operate at the latter conditions for 1h, the system was rinsed clean (under pressure) and the feed concentration readjusted to a level 2g/ℓ $NaNO_3$.

7.2.2.4 Removal of preferential depository layers

In order to remove the dual-layer, the pH of the circulating feed water was first increased to a value of 11 with NaOH to remove the polyelectrolyte. After 1 hour of operating under these conditions, the system was rinsed clean, and the pH adjusted to a value of 1 with HNO_3, to depolymerize and remove the hydrous zirconium oxide base-layer, also a one hour operation.

7.2.3 RESULTS AND DISCUSSION

The flat polymeric CA/CN micro-filters (Millipore), usually employed as substrate membranes for experimental work, have average pore-diameters of about 0,5μm. The pore sizes of the tubular CARRE sintered stainless steel supports, used in process application, are, on average, more than ten times larger. It was therefore reasoned that coarser, high molecular mass cut-off UF membranes would be more suitable for the application than low molecular mass cut-off membranes. As these UF membranes had estimated pore radii much smaller than those of the previously mentioned substrates, the use of precoatings of filter-aids such as diatomateous earth or carbon black was not considered.

The basis of this study was to determine whether a PES UF membrane could be used effectively as a support for dynamic membranes. In this respect, the topography and morphology of the deposition surface should be regarded as the main factors contributing to the effectiveness of a substrate. The only basis for assumption in comparing the pore size and pore size distribution of the various PES substrates, is found in the PWF and UF retention data given in Table 68.

As a first approach in the evaluation of PES UF substrates for their suitability in this application, their effectiveness in allowing the formation of a Zr-based rejection layer was first tested. Base-layer membranes were formed on different UF membranes, stripped, and reformed a number of times to determine trends and consistency in the performance of reformed membranes.

A range of UF membranes was therefore evaluated for their suitability as substrates for dynamically formed membranes. From Table 68, which shows the initial pure water flux (PWF) and UF performances of the PES UF membranes, it can be seen that the UF membranes used as substrates had widely different permeabilities to pure water. A reasonable difference is also noted between the membranes when the PVP retentions of these UF membranes are compared. However, the initial flux performance differences between the substrate membranes became less apparent after a number of inorganic, Zr(IV)-based, membrane-formation and stripping cycles. (See Figure 42). After stripping of the final dual-layer Zr/polyelectrolyte membrane, there was little difference between the water permeation rates of the various substrate membranes. All the membranes showed a steady decline in flux, which may have been due to compaction caused by the high operating pressure, or use of an inadequate cleaning regime during the membrane stripping cycle. (The reason for this was, however, not investigated during this initial screening exercise).

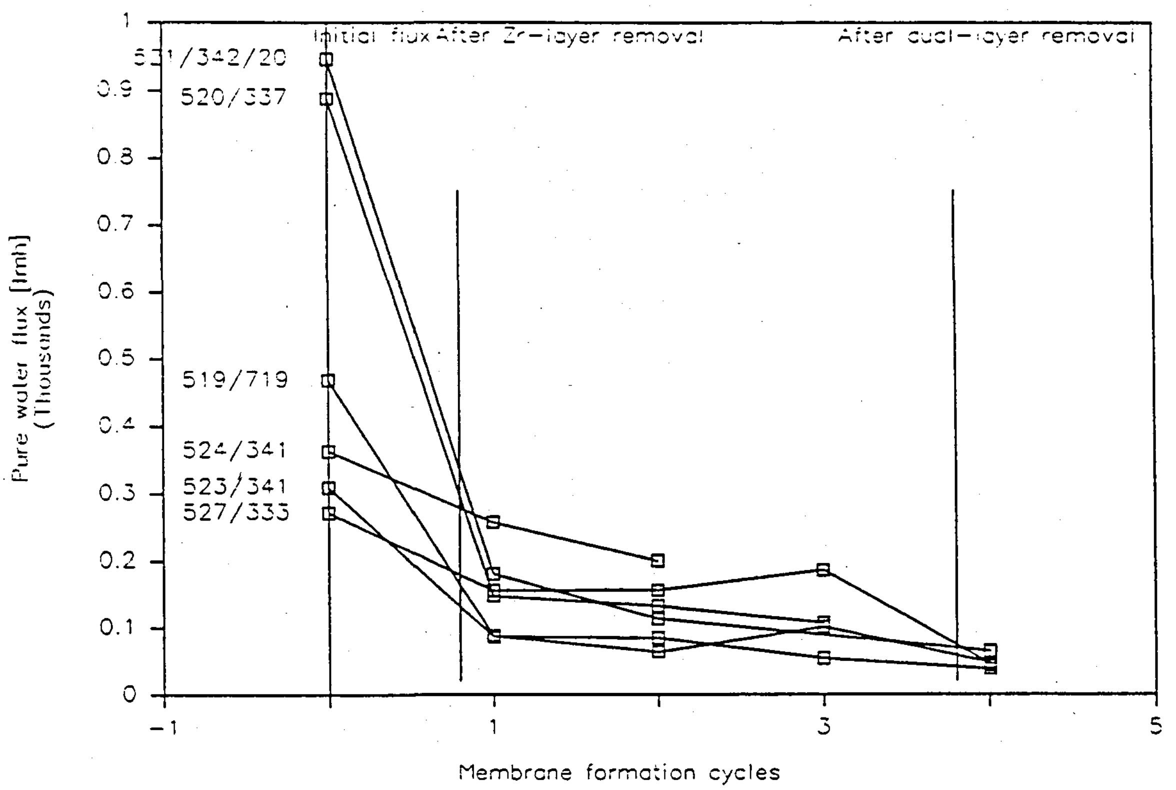


FIGURE 42:

Pure-water flux decline of UF PES substrate after stripping of the base and dual-layer dynamic membranes

The salt-retention performances of the dynamically formed Zr-base membranes are compared in Table 69. No substrate membrane replacements were made during each series of Zr and Zr/polyelectrolyte membrane formation and stripping cycles performed on each individual set of PES UF membranes.

TABLE 69:

Retention and permeate flux performance of Zr-oxide base-membranes (after repeated formation and stripping cycles) and dual-layer membranes formed on UF substrates

Polyelectrolyte Membrane code	cycle number	Formation Retention [%]	Formation Flux [lmd]	Base membrane Retention [%]	Base membrane Flux [lmd]	Dual-layer
528/723	1	18,2	7 123			
	2	17,8	7 922	46,5	3 080	AVOH7**
521/342/10	1	45,0	4 669	67,5	3 069	AVAC7**
527/333	1	40,5	14 286			
	2	36,2	16 227			
	3	35,0	15 282			
	4	39,3	14 739	83,8	2 790	PAA
527/333*	1	39,2	15 574			
	2	42,4	17 039	79,8	3 477	PAA
527/333*	1	41,1	15 951	77,4	3 794	AVOH7
523/341	1	40,3	12 355			
	2	32,1	10 987			
	3	44,0	8 543			
	4	43,4	8 348	77,4	2 256	PAA
(Membranes stored damp for 7 days)			64,0	3 700		
519/719	1	28,9	14 412			
	2	28,2	15 143			
	3	38,3	11 354			
	4	29,1	12 347	73,4	3 369	AVOH7
520/337	1	26,8	13 164			
	2	11,2	14 141			
	3	33,8	10 987	76,8	2 557	AVOH7
521/342/20	1	39,0	12 680			
	2	40,1	13 609			
	3	35,0	12 025	76,1	2 861	AVOH7
524/341	1	37,8	17 554			
	2	37,4	14 608			
	3	35,6	14 682			
	4	40,8	14 770	77,6	1 022	PAA

* Note: Membrane formation procedure repeated on unused 527/333 IPS substrates

** Note: Non-commercial polyelectrolytes

In Figures 43 and 44 the salt retentions and fluxes of the various dual-layer polyelectrolyte membranes are plotted against the PVP retention of the UF substrate membranes. Although three different polyelectrolytes were used in the preparation of the various dynamic membranes, it appears as if better salt retention performance resulted when the membranes were prepared on lower retention Kollidon 30 UF substrates. However, these results are in no way conclusive.

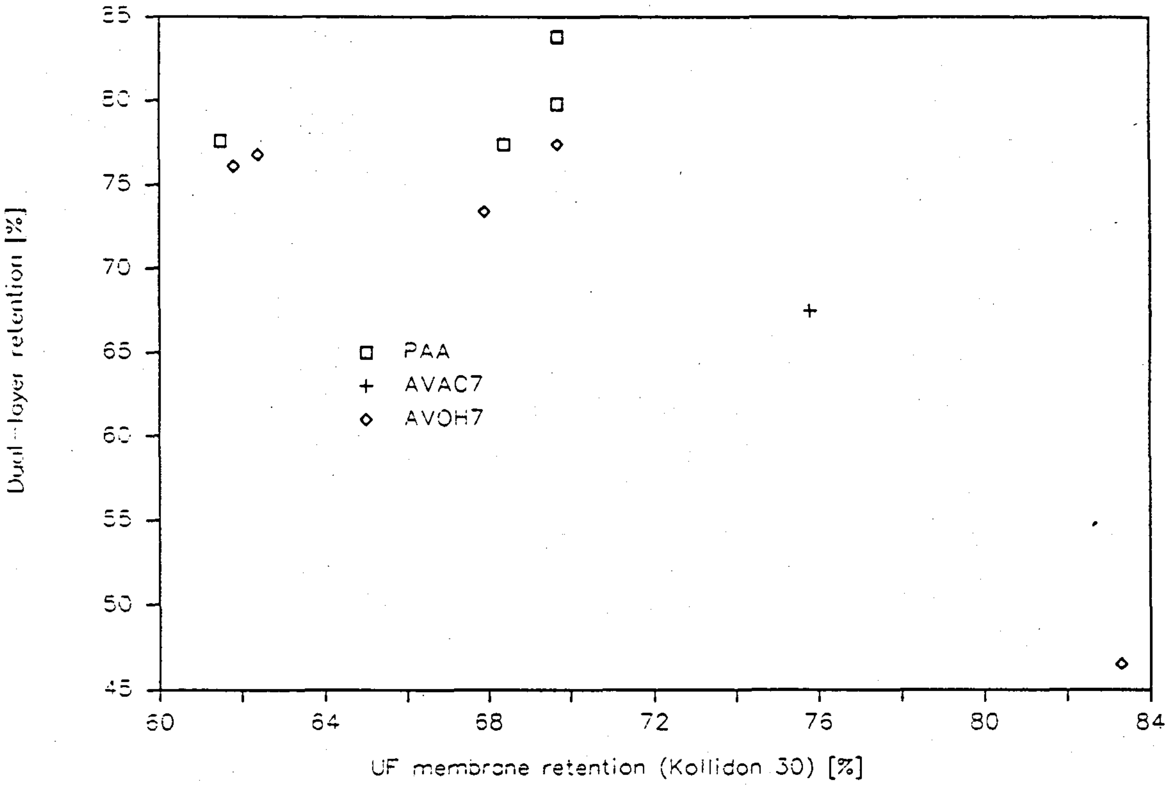


FIGURE 43:
Salt retention of dual-layer membranes versus PVP retention of UF substrate

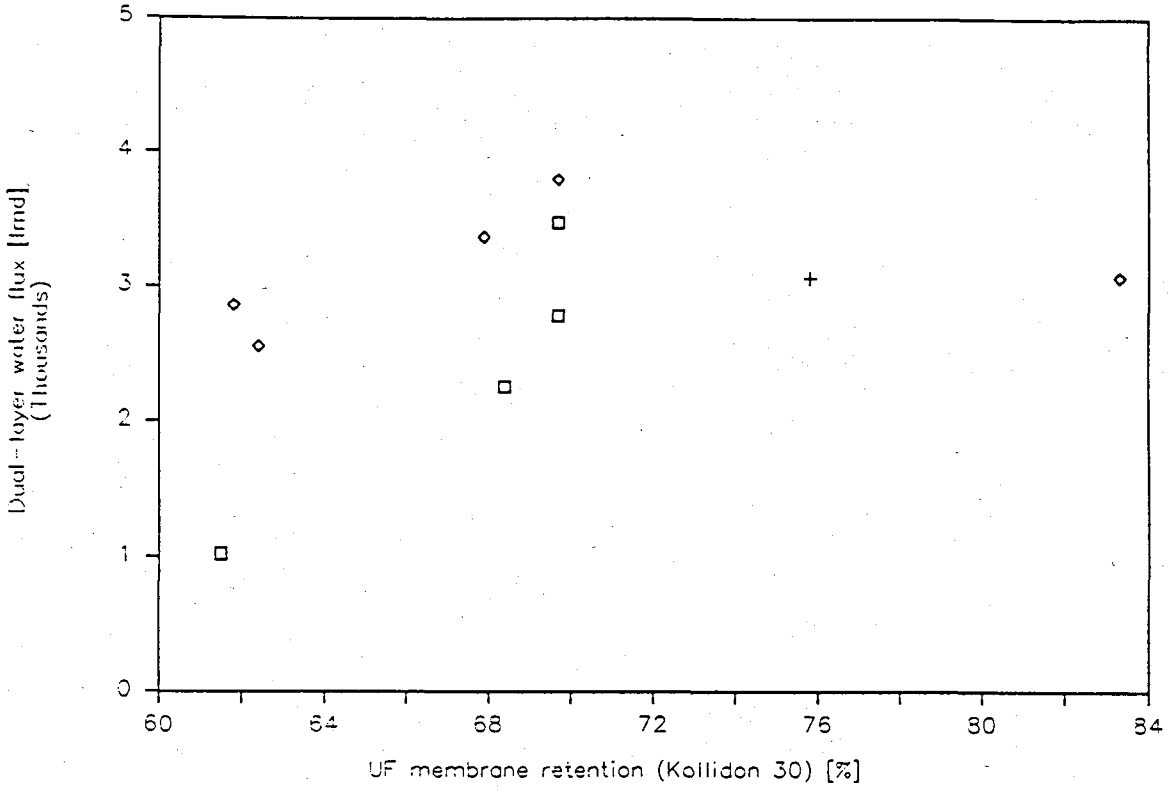


FIGURE 44:
Flux of dual-layer membranes versus PVP retention of UF substrate

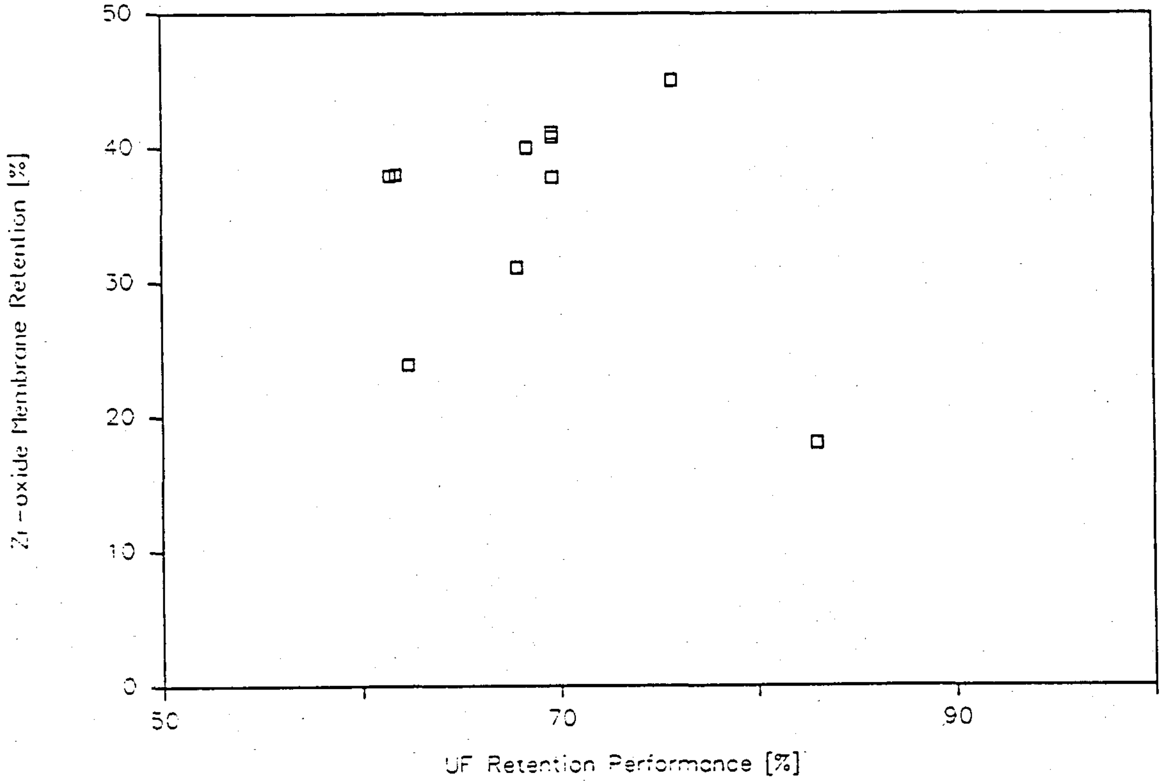


FIGURE 45:
Salt retention of Zr (IV) membrane versus PVP retention of UF substrate

Reasonably consistent retention data was observed for both Zr-oxide and dual-layer polyelectrolyte membranes, under moderate formation pressures and velocities.

7.2.4 CONCLUSIONS

Dynamic UTF membranes have been formed, with reasonable success, inside 12,5mm microporous PES substrate membranes. Some of the results are summarized below:

1) 30% $NaNO_3$ rejection at pH 7 has been obtained repeatedly with membranes formed at linear formation velocities of 1,5m/s and 2MPa feed pressure in 6 x 1m test sections with inorganic zirconium base-membranes.

2) Steady-state pure-water flux performance (200kPa, 0,5 m/s) of the substrate-membrane is reached after 3-4 inorganic base-membrane formation and stripping cycles.

3) Dynamic UTF membranes with 60 to 70% $NaNO_3$ rejection performance (2MPa, 1,5m/s, pH 7) have been formed in 6 x 1m test sections on 30% $NaNO_3$ rejection zirconium base-membranes. (These results compare well with those of control membranes formed inside 2 x 1,5m tubular porous stainless steel (Carre) substrates).

4) The $NaNO_3$ retention (pH 3,5) of the first single-layered Zr-membranes ranged between 22% up to 42%, on occasion, for the different substrates tested. Average retention values of 39% was easily obtained on "re-membraning" the various substrates evaluated.

5) The salt retention of dual-layer membranes did not differ much for substrates with 80% MMCOs between 6 000 and 40 000 dalton (evaluated against PEG and PVP). The highest point-reading for dual-layer membrane retention was 82%, and that was achieved on both extremes of the above range.

6) Some correlation was found between the 3MPa permeate flux of the first Zr-layer deposited and the UF characteristics of the substrate. All permeate fluxes, however, showed a steady decline after each re-membraning step. After four Zr-membrane replacements, the initial correlation observed had disappeared.

7) The dynamic membrane layers were *dynamic* in the sense that some loss (10% and greater) of membrane properties were observed over periods of between 18h and 67h of operation on fresh $NaNO_3$ solutions. (All evaluations were performed in close-loop tests systems).

The experimental results show that synthetic UF membranes can be used as substrates for dynamic membranes. The possibility of achieving still higher salt retention with lower cut-off Kollidon 30 UF membranes needs to be investigated.

The consistency in performance of the dynamic membranes formed was good, although a constant reduction in PWF was noticed after each membrane stripping cycle. However, it appeared as if asymptotic values are reached after a number of formation and stripping cycles.

A problem in the use of these membranes stemmed from the use of polyester as a support material for the UF membrane since hydrolysis of the polyester at the high pH-levels prevailing during membrane stripping cycles can cause weld-seam failure. However, no problem has been experienced, to date, at the low pH conditions that prevailed during Zr formation and stripping.

7.3 TUBULAR MEMBRANE-SYSTEMS DEVELOPMENT

7.3.1 BACKGROUND

This topic relates to the fluid dynamics and mechanical aspects of the design of a robust and inexpensive module to house the tubular substrate membranes. In principle, such a module should be capable of being operated continuously at both high temperature (>80°C) and high pressure (>8MPa).

Experimental results obtained in the early part of this programme indicated that satisfactory dynamic membranes can be formed on flat-sheet PES substrate membranes. The inability to duplicate the formation conditions of flat-sheet membranes on the medium-flow medium-pressure tubular-membrane test equipment, was regarded as the main reason for the reduction in performance of tubular membranes at the time.

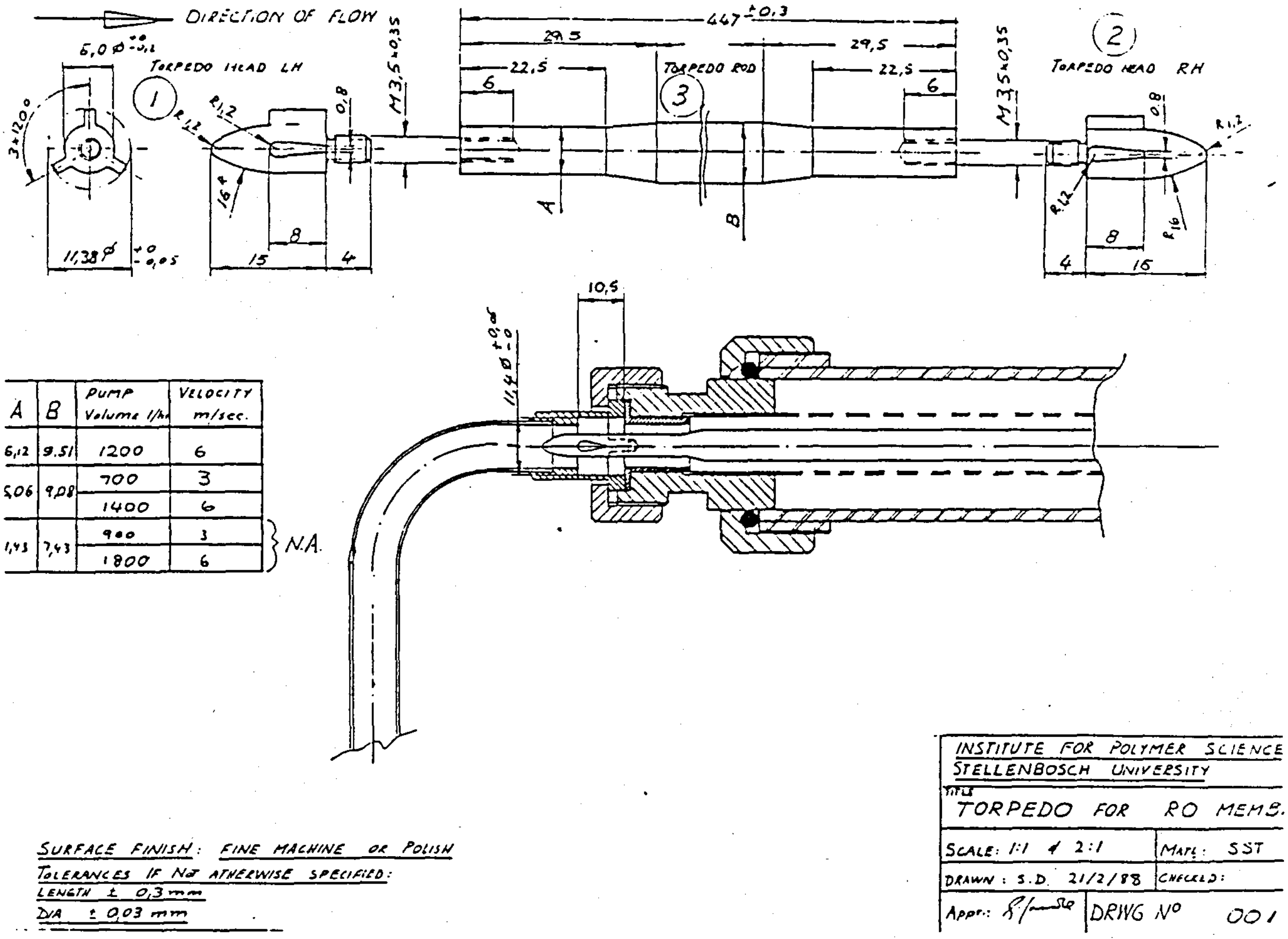
An area for innovative development would be to incorporate spaghetti-type membrane elements as turbulence promoters inside 12,7mm tubular membranes. This would lead to both an increase in membrane area, as well as a reduction in cross-sectional area.

In the text below, a technique is discussed by which small diameter membranes are cast onto the outside of a nonwoven support fabric.

However, arrangement of these membranes into a suitable flow-device was a different consideration. As a start to that programme, moulding techniques and epoxy material selection for a membrane cast on the inside of the fabric tube formed part of a parallel development programme on .

7.3.2 CASTING OF SMALL DIAMETER EXTERNAL TUBULAR MEMBRANE

The problem of increasing the linear cross-flow velocity in a test-loop fitted with 13mm tubular membranes, without increasing the pumping capacity, can be solved by fitting the membrane elements with a turbulence-promoting device. As a first approach, a membrane was fitted with a torpedo-insert (Figure 46), so that the cross-section of the membrane was altered from circular to annular.



A	B	PUMP Volume l/hr	VELOCITY m/sec.
6,12	9.51	1200	6
5,06	9,08	700	3
		1400	6
1,43	7,43	900	3
		1800	6

} N.A.

INSTITUTE FOR POLYMER SCIENCE
STELLENBOSCH UNIVERSITY
TITLE
TORPEDO FOR RO MEMB.
SCALE: 1:1 & 2:1
MAT'L: SST
DRAWN: S.D. 21/2/88
CHECKED:
APPR.:
DRWG Nº 001

SURFACE FINISH: FINE MACHINE OR POLISH
TOLERANCES IF NOT OTHERWISE SPECIFIED:
LENGTH ± 0,3 mm
DIA ± 0,03 mm

FIGURE 46:

Torpedo insert for promoting turbulence in a 13mm tubular membrane

On a test rig, which had a maximum pump capacity of 1200 litres/hour, the linear velocity could be increased from 2,64 m/sec to 6 m/sec by use of the torpedo insert in this way. The resulting higher shear rates improved the dynamic membrane performance characteristics, albeit at the expense of a greater pressure drop per unit length of membrane. To offset the disadvantage in cost of operating at a higher pressure drop, experiments were conducted to replace the insert with a porous membrane-structure so as not only to reduce the cross-flow area but also increase the packing density of a 13mm membrane module.

Below is a discussion of the design of the casting device and of the technique developed to produce a PES UF membrane on the outside of an 8mm inside-diameter support tube, fabricated from a non-woven fabric.

7.3.3 EXPERIMENTAL

7.3.3.1 Membrane fabrication: PES UF membrane on outside of 8mm i.d. support tube

A strip of non-woven membrane support fabric is fed, under constant tension, over feed and guide rollers to a mandrel. The membrane fabric is guided at an helix angle around this mandrel by means of a belt system. The belt system is driven by an electronic-controlled motor and gearbox.

The width of the fabric determines the helix angle, overlap and drive-belt width. The helix tubular membrane winding apparatus must be freely adjustable for different diameters, pitches, coating methods and speeds. The apparatus must, as far as possible, be vibration-free and all friction and guide systems must be constant and repeatable.

The fabric strip is ultrasonically fused at the overlap, so as to form a continuous tube. The external extrusion coating-die is positioned somewhere below the point of ultrasonic fusion. The welded support tube runs through the coating solution container and annular die, whereby a film of solution of the correct thickness is metered onto the fabric surface.

The coated tube enters perpendicularly into a water tank situated below the membrane applicator. The free air travelling distance, from point of extrusion to the coagulant surface, the water temperature, purity *etc.*, are important factors which affect the final properties of the membrane. RO tap water is used as the bulk of the coagulant. The membranes are cut in 3m lengths and stored under water.

All the apparatus for the continuous external extrusion coating process are installed in a temperature- and humidity controlled laboratory.

7.3.3.2 Continuous external membrane extrusion-coating die

The coater must not be fixed rigidly onto the structure of the support tube winding equipment. The mandrel is in constant sideways tension caused by the driving belt that feeds the fabric down its length, and any small variation in the tension under which the fabric is dispensed, would therefore be transferred to the mandrel. This would lead to lateral small-degree movement of the mandrel, and if the coating-die were rigidly fixed, uneven extrusion-coating of the membrane solution would result.

In the first prototype design, the external coating device consisted essentially of two parts. In this design (Figure 47) the extrusion-coater rests on a base which is fixed onto the tube-winding machine. The base is provided with small-diameter air escape-holes. An air-cushion is therefore provided for the film-coater so that it can move, without any interference of friction, freely in the plane.

Further, a deflector plate, attached to the bottom stem of the coater, directs air away from the coagulation bath surface to prevent undue disturbance of the quench-line as this would cause marks to form on the membrane surface. Equal circumferential and longitudinal coating thickness are assured by the floating and self-aligning die.

The thickness and smoothness of the coating depends on the radius of the die entry zone, the lead-in taper, land length, die clearance and surface finish. The viscosity of the coating solution must be taken into account in the design of the die. Aluminium was used as the material of construction.

A glass hopper, sealed by an O-ring to ensure easy removal and cleaning, holds the coating solution. A variable-speed metering gear-pump delivers the casting solution from a container *via* an in-line filter and static mixer to the glass hopper.

Mandrel

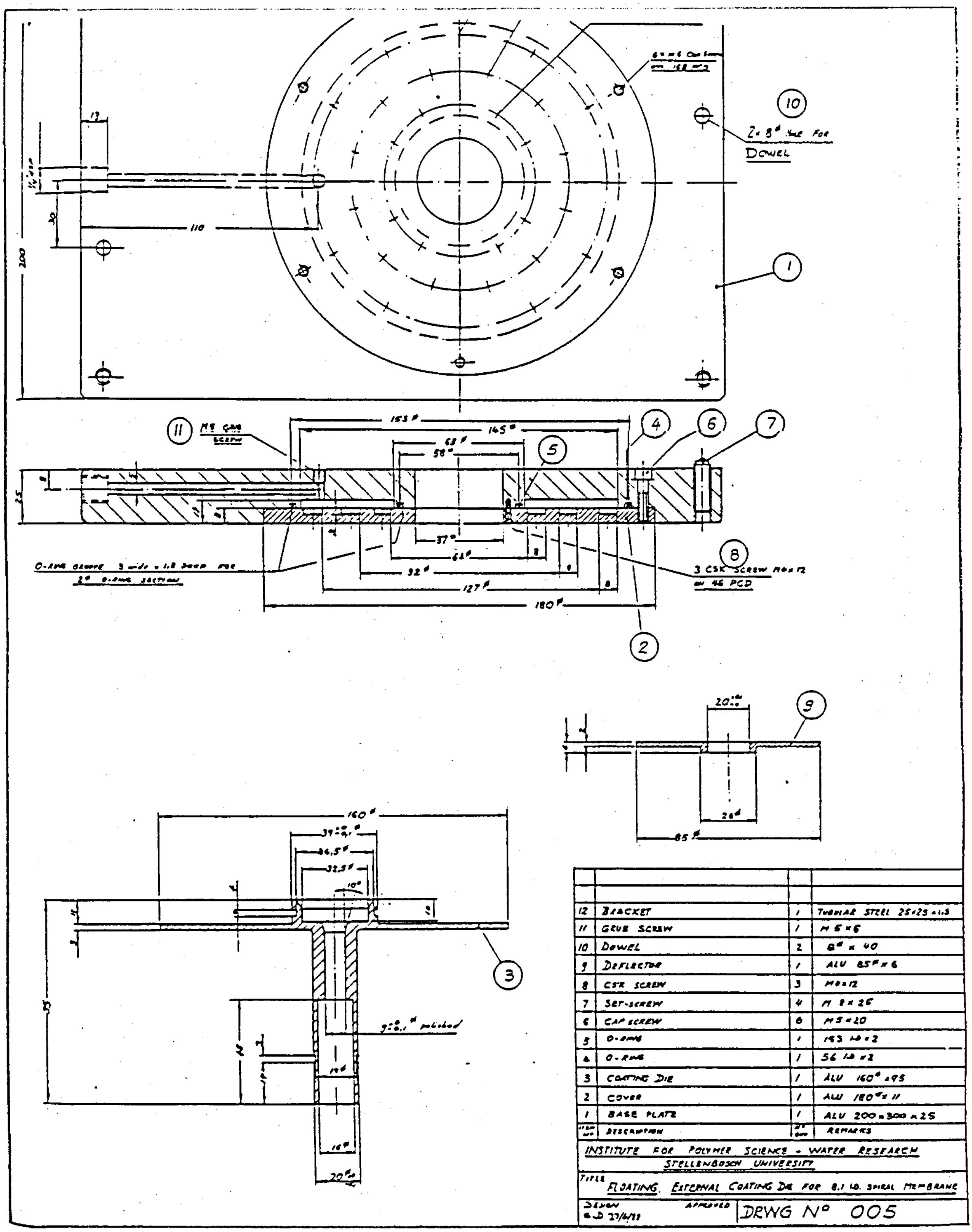
In comparison, the design of the mandrel for external coating is much simpler than for continuous internal coating, since multiple-flow channels for the casting solution and air feed and return need not be provided.

7.3.4 RESULTS

The experiment to produce tubular external membranes on a non-woven fabric proved successful.

With certain casting solution formulations, however, stress caused by contraction of the membrane during coagulation led to the formation of tiny disruptions in the otherwise homogeneously smooth membrane surface. By and large, the quality of the membranes produced in this fashion appeared to be good from microscopic analysis of the membrane structure.

During the initial stages of development, it was soon learnt that the coater was not always capable of self-alignment, and coatings of uneven thickness occurred frequently. In the design discussed earlier, much reliance was placed upon i) the viscosity of the casting solution and ii) the flexibility of the uncoated tube-section (*i.e.* section between the coater and mandrel-tip), to prevent the tube from scraping against the sides of the die when the mandrel flexed. To solve this problem, a gyroscopic system was constructed and the coater was mounted onto this device. The whole assembly rested on the air-cushion, so that total freedom of movement of the coater was ensured. No further problems of misalignment arose.



12	BRACKET	1	TUBULAR STEEL 25×25×1,5
11	GRUB SCREW	1	M 5×6
10	DOWEL	2	8ø × 40
9	DEFLECTOR	1	ALU 85ø × 6
8	CSK SCREW	3	M4×12
7	SET-SCREW	4	M 8 × 25
6	CAP SCREW	6	M5×20
5	O-RING	1	153 ID × 2
4	O-RING	1	56 ID × 2
3	COATING DIE	1	ALU 160ø × 95
2	COVER	1	ALU 180ø × 11
1	BASE PLATE	1	ALU 200×300×25
ITEM NO	DESCRIPTION	NO OFF	REMARKS

INSTITUTE FOR POLYMER SCIENCE - WATER RESEARCH
STELLENBOSCH UNIVERSITY

TITLE FLOATING EXTERNAL COATING DIE FOR 8.1 ID. SPIRAL MEMBRANE

DRAWN E.D 27/4/88 APPROVED DRWG N° 005

FIGURE 47:
Design of the external membrane applicator

Evaluation of the cast membranes proved to be a problem. PVC tubing of 8mm outside diameter, fitted with 0,2mm permeate holes was used as the internal pressure-support for the externally pressurized membranes. The supported membrane was fitted into a test cell which consisted of two 12mm T-pieces, mounted on either side of a 12mm diameter straight section of tube. The protruding ends of the membranes were sealed onto the T-pieces by means of compressed o-rings. Few membrane sealing problems arose. However, the extruded rigid PVC tube had unequal wall thickness which, without fail, led to collapse and failure of the pressure support at operating pressures of 3 000kPa. No dynamic membrane performance data were therefore gathered during the period of development of the casting equipment.

7.3.5 CONCLUSIONS

A higher cross-flow velocity can be achieved in tubular membrane modules with the present design of the test cell and pump capacity by fitting a torpedo device inside the membrane element; the membrane cross-section flow geometry is thus altered from circular to annular. The higher shear rates caused by the increase in velocity leads to the formation of dynamic membranes with improved performance.

The feasibility of casting externally coated tubular membranes was demonstrated. Efforts thus far to incorporate these membranes into a module design were unsuccessful to date.

Further it must be accepted that fouling of the annular flow channels is more likely to occur compared to circular flow-paths due to uneven flow distribution, and also that the pressure drop will be higher. In long modules fluttering of the membrane-inserts could possible lead to damage of the membrane surfaces.

Type 304 stainless steel is not suitable for machining small-diameter mandrels because of its inherent lack of rigidity. A high alloy, prehardened tool steel like 40 Cr, Mn, Mo 86 to DIN 12312 nearly has twice the tensile strength of 1 080 N/mm^2 compared with that of 304 SST of only 600 N/mm^2.

Because of the lack of rigidity of the 8 mm mandrel, the mandrel deflects and the extrusion coating die needs selfaligning for deviation from the perpendicular plane. This can be done only if a type of gyroscope housing is used for the die, which is then mounted on the floating self-aligning and self-centering base. Free movement, self-centring and self-aligning in all three axes was achieved with this combination.

Testing of 8 mm externally coated membrane on its own was difficult. Perforated internal sleeves are needed to support the membrane. PVC was used initially but proved to be unsuitable in the long term, as this material became distorted under the operating pressure due to creep. A satisfactory support medium could however be of design similar to the internal support of the early rod-like or spaghetti-type membranes.

The work was concluded at this stage because of the inability of the PET substrate material to withstand the harsh cleaning and stripping regimes of the polyelectrolyte and Zr (IV) membrane layers.

Initial research results with PES substrate membranes indicated a direct relationship between the linear cross-flow velocity and salt-rejection performance of dynamic membranes. The large pumping capacity (>4m/s) and high operating pressure (4MPa) requirement for dynamic membrane formation, imposed by the use of 12,5mm ID tubular substrate membranes, make smaller diameter membranes a research alternative. The use of turbulence promoters is another area of research that needs attention. By installing a turbulence promoter inside a 12,7 x 500mm substrate membrane, the salt rejection performance of the dynamic membrane could be increased to 91,8%.

Tubular poly(acrylic acid) dynamic membranes, formed on 500mm PES substrate membrane test sections, are now showing 85% and higher percent salt-rejection. Membranes can be stripped and regenerated without loss in flux performance. In some tests over 90% salt rejection has been obtained with the use of turbulence promoters (3MPa, 2 000 $NaNO_3$).

7.4 EXPERIMENTAL MODULE DESIGN - LOW PRESSURE DYNAMIC

Membrane modules for the laboratory evaluation of 9mm tubular membranes is discussed. Attention is given to some of the epoxy casting techniques used.

7.4.1 INTRODUCTION

The original approach of Membratek (Div. Bintech Pty.) to encase the tube-ends of 9mm self-supporting membranes in an epoxy casting (interconnecting the tubulettes with 180° return-pieces to obtain a series-flow arrangement), was used to evaluate low-pressure 9mm RO membranes. The modules are operated at a maximum feed pressure of 500kPa (20°C), as the membranes have no external pressure support except the polyester fabric onto which the membranes are cast.

The performances of the low-pressure 9mm membranes are measured against a feed solution concentration of 2g/ℓ, which, in the case of NaCl, is equivalent to an osmotic pressure of approximately 80 kPa. The effective nett pressure under which the membranes operate is therefore significantly lower than 500kPa, especially in the case of a high NaCl retaining membranes. Membrane flux is directly related to the hydrodynamic feed pressure by the following relationship.

$$\begin{aligned} Q_W &\propto (\Delta P - \Delta \Pi) \\ &\propto (P_C - P_P) - (\Pi_C - \Pi_P) \end{aligned}$$

Where

Q_W Water flux

ΔP Pressure drop across the membrane

$\Delta \Pi$ Difference in osmotic pressure across the membrane interface

Footnotes:

C Concentrate side

P Permeate side

Concentration polarization in the boundary layer on the membrane surface can lead to a further increase in the membrane wall concentration of the ionic species retained. Concentration polarization in a high-flux membrane can be reduced by increasing the linear cross-flow velocity but, however, at the expense of a decrease in the hydrodynamic operating pressure, especially in a train of series-connected modules; this is a situation hardly affordable where the nett operating pressure already is well below 500 kPa due to osmotic pressure considerations. At 0,8m/s, the pressure drop per bank of five modules of 6x400mm series connected 9mm membranes is approximately 20kPa.

To decrease the pressure drop across a bank of membranes that are being evaluated in the laboratory at higher cross-flow velocities, consideration was given to a parallel flow-through module, connecting these modules in a series arrangement. In this design, techniques were developed by which seven 9mm unsupported membranes were epoxy end-cast into a parallel arrangement, inside a class 4 PVC tube.

7.4.2 EXPERIMENTAL LAB-MODULES

7.4.2.1 Casting of 9 mm membranes into a series-flow arrangement

Casting moulds were designed and constructed for producing series modules for laboratory evaluation of the membranes. The design of the mould and materials of construction allows for easy dismantling and demoulding, and the use of releasing agents is not necessary.

The mould has two upright rods holding the membrane locating plates. The membranes are cut to length and injection moulded return-bend connectors are secured in place. The inlet and outlet to the module are plugged with a straight injection-moulded end-piece, blanked-off on the one side to prevent epoxy from entering the membrane tube. Six membranes are connected in a module in order to have the in- and outlets on the same side. The pre-assembled membrane bundle is inserted into the mould and secured in position with an elastic band.

The required volumes of the epoxy casting resin components are weighed out according to suppliers specifications, and separately heated to max. 40°C before being mixed thoroughly together. This method ensures a homogeneous mix and also reduces the curing time. (The curing time can be reduced further by exposing the casting to low humidity and elevated temperature conditions).

Once the epoxy casting has hardened, holes are machined and tapped into the casting to open the straight end-plugs to permit external connection.

Casting of 9mm membranes into a parallel-flow arrangement

Six 9mm tubes are cut to length and furnished with straight end-plugs. The tubes are fitted inside the outer PVC sleeve. The module shroud is pressed into a casting mould which has a rimmed section to locate the tubes against the inside wall of the PVC tube.

Different approaches can be used to embed the tube-ends in the epoxy casting. However, after both sides of the module had been end-capped, the module ends are machined at a 45° angle. The best machined surface finish, after a post mould curing time of 48h has been allowed, was obtained at 2 200 R.P.M.. with water as a coolant.

The modules are connected through machined end-pieces which are solvent-cemented onto the PVC shroud. The internal wetted section of the end-pieces are profiled to reduce exit and entrance pressure drop effects.

7.4.2.2 Moulding techniques

Vacuum degassing

Before casting, the epoxy solution is placed in a vacuum chamber to remove all air-bubbles from the mix.

Plunger casting

A measured volume of mixed epoxy resin is poured into the mould. The epoxy resin is forced up between the membranes by pressing the PVC tube, within which membrane bundle is housed, down into the mould up to its stop. After the expoxy had set, the procedure is repeated with the other side.

Centrifugal casting

The module is fitted with a casting mould on either end, and the whole assembly secured on top of a variable speed rotatable platform. Flexible tubes were used to connect the central casting resin reservoir, the moulds on either end of the module. Resin is dispensed into the moulds by centrifugal force.

7.4.3 DISCUSSION

Compared to the plunger approach, centrifugal casting has the advantage that both end-casings can be cast simultaneously. This saves both labour and material.

The membranes fit very tight against each other inside the PVC shroud and problems have been experienced with uneven wetting. Air, which is replaced from the fabric by the penetrating epoxy leads to the formation of bubbles, further increases the possibility of module failure.

All these problems are omitted when the centrifugal method of casting is employed.

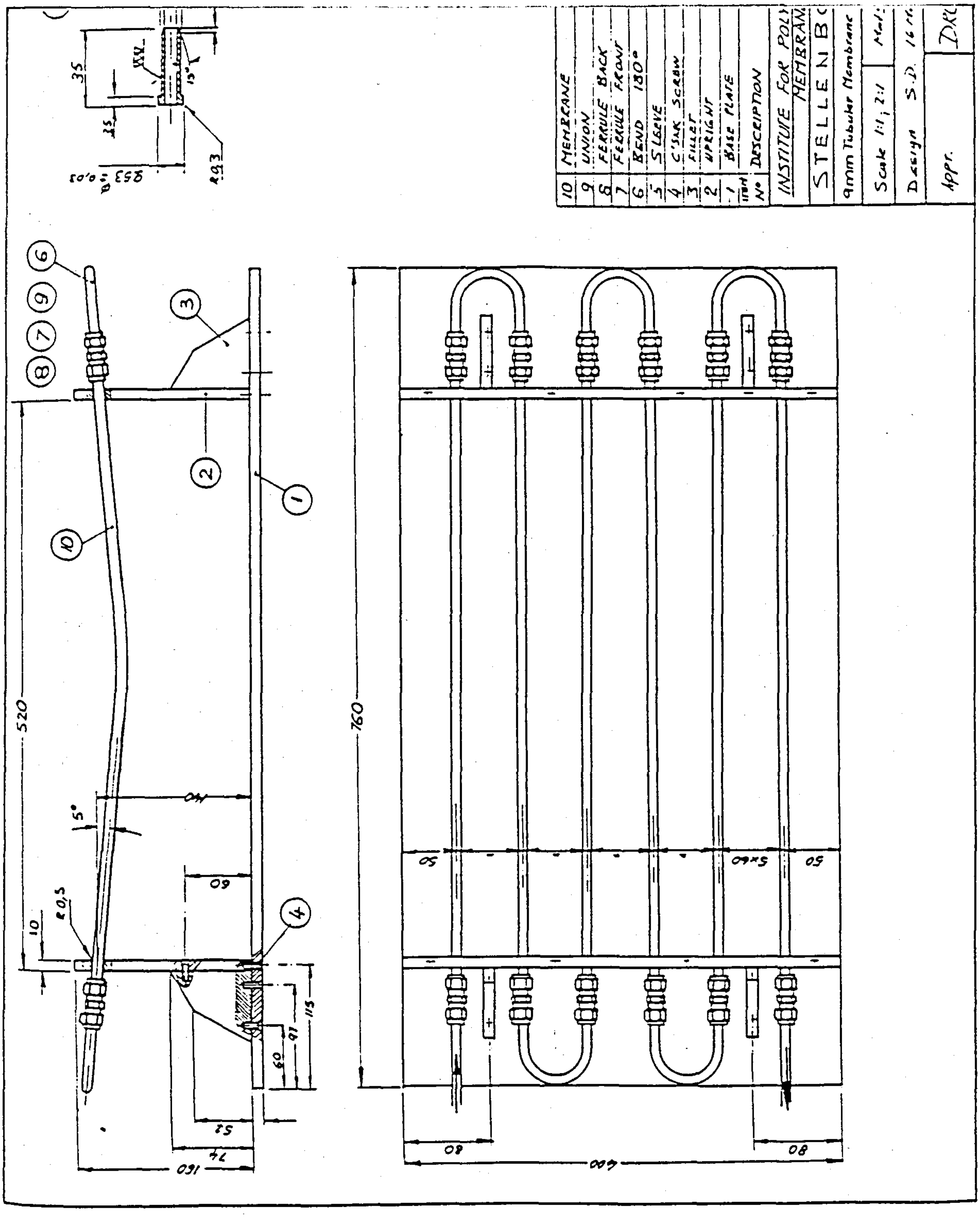


FIGURE 48:
Six-tube series-flow 9mm self-supporting test cell arrangement

Material selection of the straight stopper should be investigated to improve the bond between the epoxy and the stopper. The bond between the stoppers, presently injection-moulded from polystyrene, and the epoxy in use is not good, and frequent delamination occurs when the end-sections are machined.

7.5 CONCLUSIONS

Although the work on the dynamic membrane module development was curtailed as result of the inability of the PET substrate material to withstand alkaline membrane stripping operating conditions, much of the know-how developed could be applied in other areas of the programme. Some of the techniques used in the end-potting of tubular membranes, for example, was initially applied in the fabrication of capillary membrane modules.

SECTION 5

8. ESTABLISH PRODUCTION TECHNIQUES FOR THERMAL PHASE INVERSION MEMBRANES

8.1 INTRODUCTION

One of the main objectives of this work was to develop a membrane casting-solution system amenable to thermal phase inversion membrane preparation. Such casting systems do exist in the patent literature for polyolefinic materials such as polyethylene and polypropylene, acrylates such as polymethyl methacrylate and even fluoropolymers such as polyvinylidene fluoride. However, the literature did not report on any successful attempts in producing useful membranes prepared from the polysulphone family of materials by means of the thermal inversion process.

8.2 THERMAL-PHASE-INVERSION SOLUTIONS

8.2.1 POLYSULPHONE

No reference could be found in the patent literature with respect to thermal-inversion casting-solution formulations for polysulphone materials. Research work began with screening the solvents reported in the literature to be swelling agents for the polymers, but not true solvents. The work also involved evaluation of solvent mixtures. Little progress was made during the first period of the investigation.

Later, it was discovered that sulfolane acted as a theta solvent for polysulphone, *i.e.* it did not dissolve the polymer at room temperature, but would swell the material at higher temperatures. At much higher temperatures (>100°C) the polymer would dissolve. When a solution of the polymer in the solvent was cooled down (<90°C), the polymer would precipitate from solution, very much as was required from a thermal inversion formulation. Unfortunately the honey-comb structures that were obtained did not seem to have the inter-connecting pore-structure sought. This problem was overcome to some extent by the addition of other non-solvents (e.g. acetamide) to the solution, but much work still had to be done to improve the formulations, before attempts could be made to produce any quantity of membranes from them.

However, a major contribution in another area resulted from this work. It was discovered that when wet phase-inversion membranes were produced from some of the thermal-inversion casting mixtures, substantial reductions were obtained in the MMCO performance of such membranes. These membranes also showed to have reasonable product rates.

The research work towards aim 5 was interrupted at that time for various reasons, of which those below were the most important:

a) a request was received from Membratek for the development of a low MMCO PES UF membrane,

b) it proved very difficult at the time to handle and spin high temperature dilute casting solutions on the prototype spinning machine that was devised from information obtained from an Enka patent **[1]**.

c) It transpired from discussions **[2]** that wet phase-inversion membrane preparation is a more simple technique; it can give equivalent membrane structures and often better membranes than thermal inversion techniques do, and that the latter technique should be reserved for cases where the former technique is inappropriate for membrane casting.

The work that was subsequently conducted was described earlier (section 3), and it eventually culminated in the successful transfer of the production technology of a low MMCO tubular membrane to Membratek. (See Appendix 2: Development and Transfer of Technology for the manufacture of low cut-off ultrafiltration membranes.)

8.2.2 POLYPROPYLENE

The polyolefin family of materials cannot be engineered into porous membrane structures by means of the wet phase-inversion technique. There are a number of reasons why this is so. However, it has been shown that these materials lend themselves ideally to be processed into porous bodies by means of the thermal inversion technique; the successful commercialization of microfiltration polypropylene capillaries by ENKA and Memtek demonstrated this.

There are any number of membrane formulations available in the open and patent literature. Most of these make use of fatty amines as a solvent for the polymer, with additions of anti-oxidation agents, dispersing agents and even nucleating agents (to enhance crystal formation), to the solution. Casting solutions are prepared and processed at temperatures short of 200°C.

One of the main problems experienced with this thermal work, was to locate a supplier(s) for the tallow-amine solvent referred to in the literature **[2]**. Although the solvent is used in oil exploration drilling, it appears not to be available through normal commercial outlets.

During the exercise to locate a reliable supplier of the tallow-amine, it was learnt that an additive, used in polypropylene processing, and marketed by Henkel, has much the same properties as the materials referred to in the literature as latent solvents for polyolefins. Samples of this material were obtained, and tried in laboratory experiments for their suitability as components in a thermal inversion casting formulation. The experiment was a success. Sample films that were produced from the limited quantities of the material obtained from Henkel had graded porosities, which appeared to be very dependant on the rate of cooling of the hot membrane film; true to the classic definition of the thermal inversion process.

Unfortunately Henkel terminated the production of the specific grade of amine-solvent that gave the initial encouraging results. The company supplied a larger volume of the new substitute, but the material obtained was substantially different, and the same membrane structures could not be duplicated. A new suitable commercial supplier and recognized solvent therefore needs to be found before work can continue.

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SECTION 6

9. FABRICATION TECHNOLOGY FOR CAPILLARY MEMBRANES: PP AND PES TUBULETTES. 0,5 TO 2 mm ϕ MICROPORE (0,02 - 0,01 μm)

Much ground has been covered with regards to Aim 6 of the programme, and the establishment of equipment and protocols for producing wet-phase inversion membranes, as opposed to Aim 5. This is fortunate, as some of the equipment and techniques developed are ally to both wet and thermal inversion approaches of membrane production.

CAPILLARY MEMBRANE TECHNOLOGY - WET PHASE INVERSION

9.1 BACKGROUND

Capillary membranes (narrow diameter hollow tubes) are spun by extruding a membrane-forming solution through an annular die, which contains an exit port for the solution and a center port for metering the core- or lumen-forming medium. When the wet-jet technique is used, a non-solvent coagulant is metered into the lumen of the nascent membrane which acts both to keep the lumen from collapsing, and which initiates the coagulation process that leads to the formation of the membrane. When the dry-jet technique is employed, a gas is introduced into the center-bore to prevent collapse of the capillary. In both instances the external side of the membrane is coagulated in a non-solvent.

By adjusting the casting solution formulation and the coagulation process, membranes can be produced that are i) internally or externally skinned, have ii) dense or honey-comb substructure morphologies, are iii) ultra- or microfilters. These membranes are finding increasing application in the separation of solutes, both in the UF and microfiltration spheres of operation. Membranes of this type are pressurized both from the inside or the outside, depending on wall thickness and external diameter. The operating pressure of the membranes normally does not exceed 2-4 bar.

Very rewarding and successful attempts have been made over the contract period to produce these membranes, by employing the wet-jet technique of fabrication. The membranes are self-supporting at 2 bar (some with burst pressures up to 12bar), and are being evaluated in a module by epoxy-casting a bundle of the capillaries into a plastic sleeve. The external diameter of the membranes are in the one to two millimetre diameter range.

9.2 EXPERIMENTAL

9.2.1 MEMBRANE FABRICATION EQUIPMENT

The prototype equipment (see Figure 49) used to spin 'wet-jet'-type membranes was not elaborate, and essentially consisted of the following:

a) A precision-gear metering pump to dispense the membrane solution to the

b) Spinning die.

b) The core-fluid was dispensed from a Mayottereservoir, and the rate of flow was controlled by means of a micro-needle valve and manometer.

c) The membranes were extruded into a shallow tank which contained the external coagulant.

d) Draw-off and take-up devices are used.

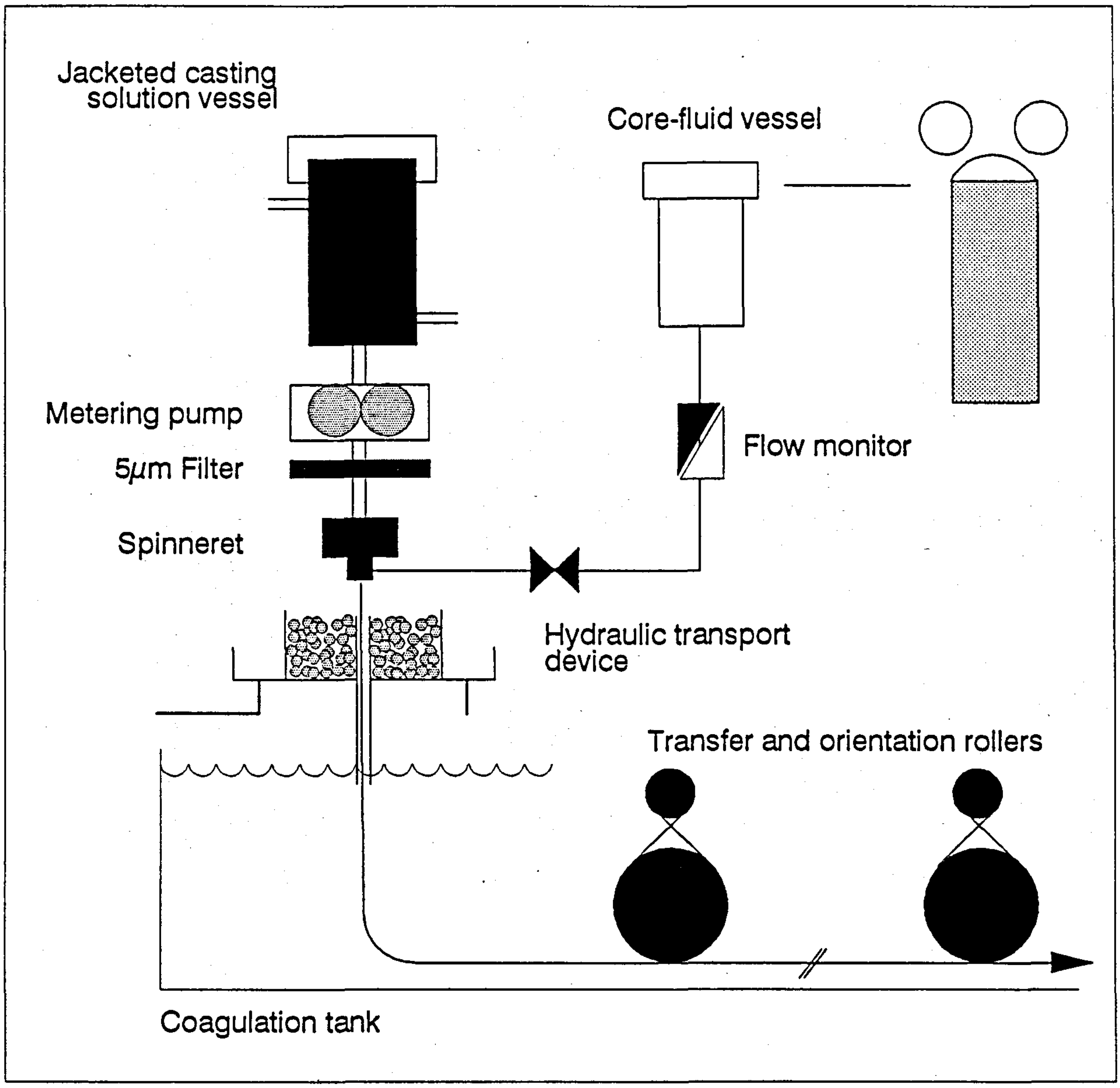

FIGURE 49:
Prototype equipment used to spin "wet-jet" membranes

A different approach may be adopted to facilitate the production of dry-spun membranes. The prototype apparatus designed and built is furnished with electrically driven draw-off rollers, but the design is also such that the membrane is spun into an 8 mm tube (2 metres long) through which coagulant flows continuously downwards under gravity. This method allows both for a high membrane production rate (1,8 m/s), as well as draw-down of the liquid extrudate to diameters very much thinner than the original orifice size of the spinneret. Trial runs have been conducted on this equipment.

The many teething problems encountered on this machine were all magnified by the high rate of membrane production. The construction of a second prototype (unsophisticated scale-down version with a shorter down-pipe and a manually operated take-up device) proved a way out to allow some experience to be gained on establishing production regimes and monitoring devices. The machine was commissioned early in February, 1988, and membranes, useful for ultrafiltration, were produced during the first trials conducted with this equipment.

These initial dry-spun membranes are externally skinned, as opposed to the internally skinned membranes produced during the wet-spun trial runs.

9.2.2 MEMBRANE MODULES

All membranes produced were initially used exclusively in epoxy resin compatibility studies. After a large number of different epoxy resins had been evaluated, an epoxy potting compound, which had a reasonably short gel-time, medium viscosity and good machineability, was selected for further trials.

Various problems had to be overcome, to reach a stage where a module product can be expected to be made reproducible. However, fair progress has been shown in the short history of the development programme, and some of these modules have actually been put to the test in the field on streams such as tap water, sea water pretreatment and cooling water blow-down streams.

The method currently adopted for producing the 600mm short-length 40mm diameter modules are as follows:

1) Membrane fibres are conditioned in a 1:1 aqueous glycerol mixture for a specified period.
2) The membranes are air-dried in an enclosed cabinet before their open ends are sealed.
3) A bundle of membranes is drawn into a PVC sleeve, into which a permeate outlet hole was pre-drilled. (This applies to internally pressurized membranes).
4) Both membrane-ends are encased in epoxy on a casting device.
5) After a specified time the moulding is removed and the ends of the membranes are machined open.
6) PVC end-connectors are solvent-welded onto the shroud-ends to complete the module product.

9.2.3 MEMBRANE EVALUATION

Membrane modules were evaluated on small low-pressure test-loops that had been constructed for the purpose. The system was operated at 2 bar pressures.

9.3 CONCLUSIONS

Although the progress to date was very rewarding, the problems that have been encountered along the route, to at least establish the technology at some level of sophistication, was trying. In retrospect, with regards the programme as set out initially; it was very ambitious. However, it brought the best from the research team.

Unfortunately, this led to some of the proposed work never receiving attention. Amongst these count

- a) the design of automatic cleaning devices,
- b) study the performance of membranes on real effluents.

However, it is only a matter of a short time, for the membrane products that stemmed from this work to operate in field trials on a continuous basis (as indicated by Membratek).

We can therefore conclude that:

a) Capillary membrane can be produced, and only need to be optimized.

b) Most of the problems still existing will concern module production, with a special emphasis on potting compounds, potting procedures and increasing fibre strength.

c) Initial tests with the capillary membranes have proved the following advantages of the system:

  - i) The membranes may be cleaned with high concentrations of NaOH because of the absence of a PET support fabric, and
  - ii) they may be made to very low MMCO specifications, because the low fluxes can be counteracted by higher surface areas, and,

d) The above aspects make it clear that capillary membranes need a high priority in any contract for the development of new membrane fabrication technology.

SECTION 7

10. MAINTAIN A WATCHING BRIEF: PERVAPORATION

The only work of consequence followed from the interest that SASOL had in pervaporation. SASOL normally used water to wash alcohols from their various hydrocarbons. Pervaporation offers an alternate route to remove alcohols from alpha olefins.

10.1 LITERATURE SURVEY

Pervaporation, a process which consists essentially of using a permselective membrane to separate compounds in a liquid mixture, was discovered in 1917 **[1]**. Initially, little research was done on this technique. The earliest work on fractionating liquid mixtures by pervaporation techniques was conducted in the mid-1950s **[2, 3]**. This process is potentially useful in all fields in which distillation techniques are difficult, such as fractionation of close-boiling components, azeotropic mixtures, and monomeric mixtures **[3-9]**. Other applications include the separation of heat-sensitive mixtures, the concentration of fruit juices **[10]**, the elimination of traces of impurities and the removal of water from an esterification reaction as soon as it is formed **[11]**.

During the past ten years pervaporation has developed from laboratory research into a large-scale industrial operation. Although today's industrial plants are concerned with the removal of water from azeotropes, dehydration of organic solvents or solvent mixtures, research and development has widened into other areas. The removal of high- and low-boiling organic substances from aqueous streams, and the separation of special compounds such as benzene from hydrocarbon mixtures, are some of the targets for the development of a new generation of membranes **[12]**.

While a considerable amount of research has concentrated on the separation of water/alcohol and water/hydrocarbon mixtures by the pervaporation process, little has been directed towards the separation of alcohol/hydrocarbon mixtures.

Since the beginning of the 1980s however, organic/organic separation received more attention **[2, 3, 6, 8, 9, 11]**. Most of this work has been aimed at the separation of azeotropes and isomers.

10.2 BACKGROUND TO RESEARCH

A project was therefore initiated to synthesize a polymer for making a membrane with which to study the separation of alcohol from the organic solvent, hexane, by pervaporation.

The objectives of this study were the following:

(a) The design and construction of a pervaporation test apparatus.

(b) The synthesis of polymers consisting of acrylic acid, vinyl acetate and hydroxyethyl acrylate with various monomer ratios.

(c) Investigation of different degrees of hydrolysis and different degrees of hydrophilicity.

(d) Characterization of synthesized polymers by means of NMR spectroscopy techniques.

(e) Making of thin-film composite membranes from synthesized polymers.

(f) Testing these membranes in the pervaporation test apparatus and evaluation of the membranes and the process on the basis of GC results.

10.3 EXPERIMENTAL

Details are contained in the M.Sc.-thesis of Ferreira **[13]**.

10.4 RESULTS AND DISCUSSION

Membrane separations should be considered as a complement to existing conventional separation operations, but are not likely to be capable of performing a complete purification and completely displacing conventional separations for any particular purification process. The separation capabilities of membranes should be examined carefully to identify the best concentration range in which to use the membrane in question. A membrane operation may be capable of performing a small portion of a total separation and greatly improving the overall process.

10.4.1 PERVAPORATION APPARATUS

Pervaporation facilities were designed and built. A schematic representation of this equipment is given in Figure 50.

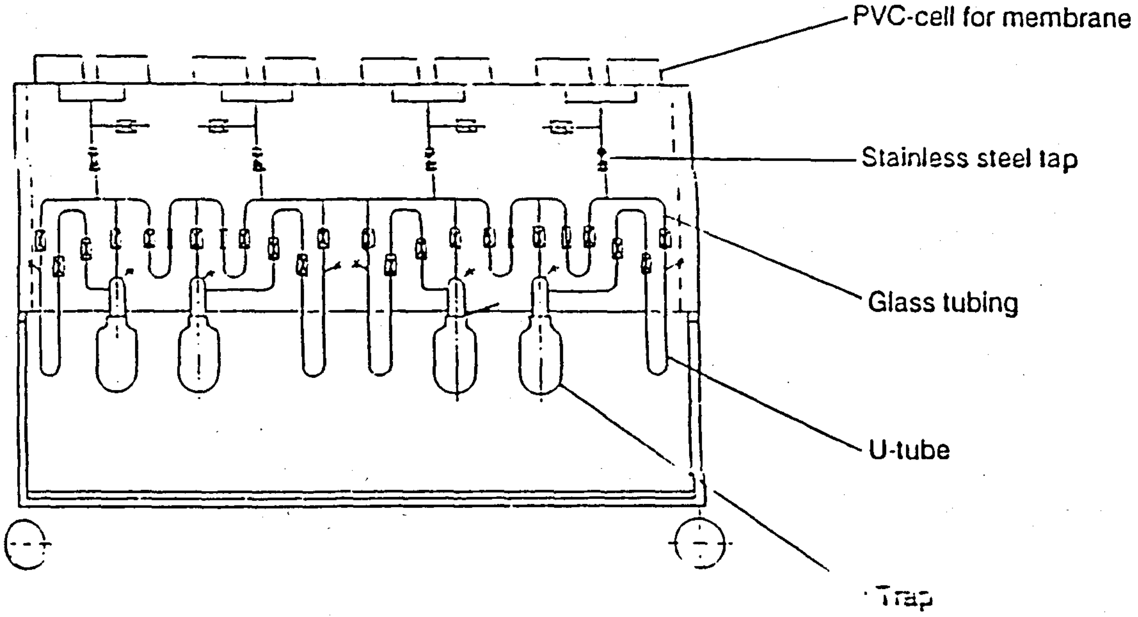

FIGURE 50:
Schematic representation of the pervaporation test apparatus

10.4.2 POLYMER SYNTHESIS

Terpolymers, consisting of vinyl acetate, hydroxyethyl acrylate and acrylic acid, were synthesized **[13]**. Four different monomer ratios were used.

10.4.3 VARIATIONS IN CHEMISTRY

10.4.3.1 Hydrophilicity

Variations in the degree of hydrophilicity were achieved by incorporating different amounts of acrylic acid in the polymer. The experimental values of amount of acid in the polymer differs from the reagent feed values. Four terpolymers, varying in acrylic acid from 0 to 15%, were successfully synthesized.

10.4.3.2 Hydrolysis

Different degrees of hydrolysis were attempted by controlling the reaction with specific amounts of sodium hydroxide. The actual hydrolysis values were determined by NMR analysis of the polymer's chemical structure.

10.4.4 CHARACTERIZATION OF POLYMERS

The characterization of the polymers was done by NMR spectroscopy. Integration was done, over certain areas, to carry out calculations.

10.4.5 MEMBRANE FORMATION

The pour-on technique was applied in membrane formation. A solution of polymer plus crosslinking reagent (H_2SO_4 or $K_2S_2O_8$) was poured onto a substrate prior to heating to 120°C.

10.4.6 MEMBRANE EVALUATION

The membranes were evaluated in terms of a percentage of ethanol in the permeate in comparison with the percentage of ethanol in the feed-mixture. These values were obtained by injecting 0,5 μl of both the feed and permeate mixtures into a gas chromatograph.

Both a 50% and a 30% ethanol feed-mixture were used for each of the membranes. The flux of the membranes was estimated, based on the amount of permeate in the trap. Each run lasted for 8 hours.

To establish the performance of the synthesized membranes, they were tested against the commercial membranes, e.g. GFT-standard, GFT-wasserreich and a fabricated Gantrez AN 119 membrane (made according to a patented literature reference **[14]**). Polyvinyl alcohol membranes with differing molecular mass (72 000 vs 15 000) were also tested. All these results have been documented, reference 13, Appendix A.

10.4.6.1 Commercial Membranes

The selectivity of the GFT-standard membrane is higher for lower amounts of alcohol in the organic media. The differences in selectivities and in flux for GFT-standard compared to GFT-wasserreich, makes it obvious that chemical modification plays an important role in membrane effectiveness. Future research into chemical modification of membranes will be very valuable.

10.4.6.2 Influence of Molecular Mass

Higher selectivity is achieved using membranes of higher molecular mass but a compromise is necessary, because flux decreases with increasing molecular mass. This only underlines the fact that future research regarding chemical modification of membranes will be very valuable.

10.4.6.3 Influence of Modification of Membrane Chemistry

Varying the chemical nature of membranes was the selected route for this research. Results had indicated that there was a need to change the chemical structure of a membrane in order to obtain the best benefit out of specific separation situations. There is obviously more benefit to be gained by further fine tuning of the membrane chemistry.

The best membrane 013:50 poly(vinyl acetate-co-vinyl alcohol-co-acrylic acid-co-hydroxyethyl acrylate) gave a selectivity average of 2 200 with a 5% ethanol feed mixture in comparison with the GFT-standard membrane that gave a selectivity of 3 300 with the same feed mixture. This membrane gave a flux of 88 kg/m^2.d in comparison with the GFT-standard membrane of 39 kg/m^2.d. The values are all calculated averages.

The terpolymer, poly(vinyl acetate-co-hydroxyethyl acrylate-co-acrylic acid) appeared to be a useful membrane material.

10.5 SUGGESTED FUTURE RESEARCH

This could involve chemical modifications around the above terpolymer structure; using substrates of fine microporosity in order to produce thinner active films; using hollow fine fibre supports to maximize surface area; using preheated feed to the pervaporation membrane; studying trace amount removal of hydrophilic substances from organic media.

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