

THE FEASIBILITY OF REVERSE OSMOSIS AS A WATER
RECLAMATION PROCESS WITH SPECIAL REFERENCE TO THE
REJECTION OF ORGANIC COMPOUNDS

by

CHRISTIAAN FREDERIK SCHUTTE

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Supervisor: Prof G. S. Hansford
Department of Chemical Engineering
University of Cape Town

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ABSTRACT

THE FEASIBILITY OF REVERSE OSMOSIS AS A WATER RECLAMATION PROCESS WITH SPECIAL REFERENCE TO THE REJECTION OF DISSOLVED ORGANIC COMPOUNDS

by

Christiaan Frederik Schutte
Water Research Commission
P O Box 824
PRETORIA 0001

August 1986

This thesis deals with water reclamation and water reuse in the South African water supply context. The overall objective of the study is to assess the potential role and feasibility of reverse osmosis as a water reclamation process. In order to achieve this objective a number of separate desk, laboratory and pilot plant studies were conducted.

It was concluded from the first desk study that a significant potential role exists for reverse osmosis in the South African water economy, mainly for the treatment of industrial effluents and, in the longer term, for the reclamation of water from sewage effluents and for the treatment of effluents and recycled water in indirect water reuse situations.

A cost analysis showed that reverse osmosis could become economically viable in some water reuse situations in the near future provided that a productive membrane life of about three years can be achieved and that membrane fluxes can be maintained at design rates. These findings indicated the need for a pilot plant study to determine the effects of pretreatment and membrane cleaning on flux levels and rejection.

A 50 m³/d pilot plant was designed and operated for a period of about six months from which it was concluded that acceptable flux levels can be maintained in tubular reverse osmosis plants treating well-oxidized activated sludge effluent with and without extensive pretreatment, provided both chemical and physical cleaning methods are employed.

The desk study on the rejection of contaminants by reverse osmosis membranes indicated the need for a simple model that can be used to predict the removal of organic compounds of interest in water reclamation applications. It was concluded from a fundamental laboratory study, which included the evaluation of existing membrane models against laboratory data, that the solvophobic theory can be adapted in a simplified form to predict the transport of dissolved organic compounds in relatively non-polar reverse osmosis membranes. Based on reverse osmosis, diffusion, sorption and desorption data a mechanism is, furthermore, proposed for the transport of phenol in different membranes.

THESIS CONTRIBUTION TO KNOWLEDGE

This thesis contributes to knowledge on the practical as well as fundamental aspects of the feasibility and potential application of reverse osmosis as a water reclamation process.

Contributions to knowledge on practical aspects are the following :

- (i) Potential applications of reverse osmosis in the South African water economy are identified for the reclamation of water from sewage effluents, the treatment and reclamation of industrial effluents, and desalination of brackish and sea water.
- (ii) The potential role of reverse osmosis in water reuse situations is analysed in terms of recycle rates and water quality. Equations are developed for hypothetical situations where water is reclaimed and reused directly, compared to situations where reuse occurs indirectly.
- (iii) The economic viability of reverse osmosis is analysed for South African conditions. Trend analyses identify the most important cost factors and quantify the effects of variations in these on the unit water cost.
- (iv) An analysis is made of the technical feasibility of reverse osmosis for water reclamation applications with respect to pretreatment requirements, membrane cleaning, membrane systems and membrane performance, based on literature and pilot plant data.

(ii)

Contributions to knowledge on fundamental aspects are the following :

- (i) From a review of membrane models, those that can be used as simple models to predict the rejection of organic compounds are identified and evaluated using experimental data.
- (ii) The solvophobic interaction theory is adapted in this thesis to describe solute-solvent-membrane interactions. This adaptation is simplified by relating the solvophobic interactions to total cavity surface area, and also to solute molecular mass. The simplified theory is developed into a predictive model by incorporating a factor based on molecular structure to account for differences in diffusion coefficients. Excellent correlations are obtained with experimental data on the rejection of a series of alkyl alcohols and a series of alkyl phenols by a composite aromatic polyamide membrane.
- (iii) Equilibrium and transport phenomena in phenol and cellulose acetate, composite aromatic polyamide and polysulphone membrane systems are quantified. Based on the experimental data a mechanism is proposed for the transport of phenol in these membranes.

EXECUTIVE SUMMARY

This thesis deals with water reclamation by reverse osmosis in the South African water supply context. The overall objective of the study is to assess the potential role and feasibility of reverse osmosis as a water reclamation process. In order to achieve this objective a number of separate desk, laboratory and pilot plant studies were conducted. The desk studies were conducted to determine the potential role and potential applications of reverse osmosis in South Africa and the economic viability and technical feasibility of the process in water reclamation applications. Based on the findings of the desk studies, pilot plant and laboratory studies were conducted to obtain data and information on certain aspects that were identified.

Potential applications of reverse osmosis in South Africa : A survey was conducted to identify areas and industries where problems with water supply and/or waste water disposal are experienced or expected and where the application of reverse osmosis or other water reclamation processes could potentially play a role in alleviating these problems. The concept of water reclamation as used herein is defined as the production of water for domestic or industrial use from (treated) waste water or from other unconventional sources including sea water and brackish water.

The main findings are :

In the short to medium term (up to about 1995) the major potential large-scale applications are projected for the treatment of industrial effluents to reclaim water for reuse and to prevent pollution of receiving waters, mainly by dissolved inorganic solids.

A number of larger towns and cities in South Africa are identified where desalination of available brackish water supplies or reclamation of water from sewage effluents can potentially play a role in the water supply. These include Beaufort West, Graaff-Reinet, De Aar, Pietersburg, the East London-King William's Town area, Cape Town, the Pretoria-Witwatersrand-Vereeniging area and the lower Vaal River supply area. (See Figure 2.5, page 2.25).

In relatively isolated areas, desalination of brackish water can potentially play a role in alleviating shortages or predicted shortages. However, since these advanced technologies are relatively costly and require expert supervision, some form of subsidization and technical support will be required.

Projections show that sea water desalination is too costly to be considered for large-scale water supply in the short to medium term.

Potential role of reverse osmosis in water reuse situations

A desk study was conducted to determine the potential role and advantages of reverse osmosis in hypothetical situations where treated effluents are reused directly and indirectly. Equations are developed for the quality of the final water supply under different treatment conditions and rates of reuse. It is shown that the potential role of reverse osmosis in a particular water reuse situation is determined by the required final water quality, the quality of the raw water source and other potential sources, and the required rate of recycling (in addition to economic and technical factors which are discussed separately).

The economic viability of reverse osmosis as a water reclamation process

This desk study was conducted in order to establish whether the estimated cost of water reclaimed by reverse osmosis is within the range where it would be economically viable to augment water supplies. The estimated cost of reclamation of R0,80/m³ is markedly higher than current costs of producing potable water from conventional supplies. However, when sources within a catchment become fully committed, and water has to be imported, it can be expected that these costs will rise to levels where reclamation becomes a viable alternative. Projected costs for water transfer schemes currently under construction show that this is already the case in certain areas.

A sensitivity and trend analysis shows that variations in the costs of membrane replacement and electrical power have the biggest effects on the unit reclaimed water cost. It is shown that the critical productive membrane life is about 2 years (Figure 2.7), below which there is a very steep increase in unit water cost. Membrane costs are determined by the water flux that can be maintained over the long term and the maintenance of membrane rejection characteristics. Information on these aspects is not readily available for water reclamation applications and in order to obtain data for further planning, a pilot plant study was initiated.

Pilot plant studies

The objectives of the pilot plant studies were to determine the effects of feed water pretreatment and membrane cleaning on flux levels and rejection over a relatively long period, and to monitor membrane performance with respect to the removal of dissolved organic substances.

The pilot plant research was carried out by the National Institute for Water Research (NIWR) of the Council for Scientific and Industrial Research (CSIR) under contract to the Water Research Commission (WRC). The author initiated this project, defined the objectives and drew up the research programmes. The author was responsible for the overall design and control of the project but the day to day running and control was conducted by the NIWR.

The pilot plant studies confirmed that acceptable flux levels can be maintained in tubular reverse osmosis plants treating well oxidized activated sludge effluent with extensive pretreatment, provided both chemical and physical cleaning methods are employed. Chemical cleaning of membranes is essential to restore flux levels while physical cleaning by means of flow reversal and sponge balls assists in preventing rapid membrane fouling. Extensive pretreatment is not necessary in a once through plant employing flow reversal, provided linear flow velocities are kept above 0,7 m/s. In a tapered flow plant, advanced pretreatment appears to be necessary in order to prevent excessive fouling of membranes in the last stage.

The rejection characteristics of some of the membranes in the pilot plant deteriorated prematurely due to undefined reasons. It appears that a combination of factors including (a) conditions during chemical cleaning (b) residual chemicals from pretreatment and cleaning and (c) the concentration effect of the tapered plant configuration contributed to the degradation of membranes in the last stage of the plant.

A very good quality reclaimed water can be produced in terms of potable water standards. Post-treatment will, however, be required as a final disinfection barrier and for the removal of very small residual amounts of organic compounds.

It was concluded from the results of this and a parallel study by the Municipality of Port Elizabeth that an economically acceptable membrane life can be achieved, provided that the use of pretreatment and cleaning chemicals is very closely controlled.

Literature and experimental studies on the rejection of dissolved organic compounds by reverse osmosis membranes

It was concluded from the literature study that dissolved organic material is very effectively rejected by reverse osmosis membranes. However, some compounds, mainly low molecular mass, relatively volatile organics do permeate the membranes. As some of these compounds have been identified as suspected carcinogens, it is considered important to investigate the factors that affect the removal of dissolved organics by different membranes.

The objectives of the laboratory study were, therefore, to identify and determine the effects of equilibrium and transport phenomena on the rejection of dissolved organics, to identify or develop simple models that can be used in water reclamation applications to predict the rejection of organics of interest, and to evaluate such models against experimental data.

From a review of membrane models, those that could be used as simple predictive models were identified and evaluated against experimental data. These models did not comply fully with the requirements of this study. It was, therefore, decided to adapt the solvophobic theory in a simplified form for solute-solvent-membrane interactions, based on Belfort's (1984) adaptation to activated carbon adsorption reactions. It is shown that the total cavity surface area can be used instead of the nett free energy change in associa-

tion reactions such as the sorption of a solute from solution by a membrane. Transport effects are incorporated in the model through a factor based on molecular structure to account for differences in diffusion coefficients. Excellent correlations are found with experimental data on solute transport and total cavity surface area, corrected by the hydrodynamic factor, for a series of alkyl alcohols and alkyl phenols and a composite aromatic polyamide membrane. This model is further simplified by relating total cavity surface area to molecular mass and molecular structure. In this form the model complies with the requirements of this study.

The effect of equilibrium and transport phenomena on the rejection of phenol by different membranes was studied in detail. Sorption, desorption and diffusion studies were conducted and from the results it is concluded that the interaction between phenol and the composite polyamide membrane is stronger than between phenol and the cellulose acetate membrane, resulting in a larger degree of sorption, stronger attractive forces, lower rates of diffusion and therefore good rejection of phenol by the composite membrane compared to poor rejection by the cellulose acetate membrane.

Conclusions and recommendations

These studies confirm that a significant potential role exists for reverse osmosis in the South African water economy and that the process is technically feasible and economically viable in water reclamation applications. Furthermore, that the simple model based on the solvophobic theory can be used to predict the rejection of alkyl alcohols and alkyl phenols by relatively non-polar membranes.

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It is recommended that experimental data be obtained for a wider range of organic compounds in order to evaluate the model on a more general basis.

Furthermore, that a relatively small, say 500 m³/d, reverse osmosis plant be constructed in a practical water reclamation application in order to verify the pilot plant findings and to obtain design and operating criteria for large-scale applications.

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Dedication

Ek dra graag hierdie tesis op aan Henriette, Isalde, Surette en Chris vir hulle liefde en ondersteuning.

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APPENDIX C : PUBLICATIONS

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NOMENCLATURE

a_i	chemical activity of component i in solution.
A	water permeability coefficient.(cm/s. kPa)
A	molecular surface area.(nm ²)
A_{xs}	cross-sectional area
A	electrochemical affinity.
B	solute permeability coefficient.(cm/s.kPa)
C_f, C_p	concentration of solute in feed and product. (mmol/ℓ, mg/ℓ)
C_s	concentration of solute.(mmol/ℓ, mg/ℓ)
C_{wm}^1, C_{wm}^{11}	solute concentration in membrane skin and porous support respectively. (mmol/cm ³ , mg/cm ³)
C_w'	equilibrium water content of the membrane surface. (mmol/cm ³ , mg/cm ³)
D_s, D_w	solute and water diffusion coefficient respectively. (cm ² /s)
D	Clausius-Mosotti function.
$\frac{DAM}{K\bar{\epsilon}}$	solute transport parameter in preferential sorption-capillary flow model.(cm/s)
E_{ij}	molar interaction energy. (kJ/mmol)
$E_s, \Delta E_s$	Taft steric constant.
ΔE	energy of vapourization,(J /mmol)
f_{ij}	friction coefficient between components i and j .
F_{ij}	frictional forces.
ΔG_{cav}^{nett}	standard free energy change of cavity formation. (kJ/mmol)
ΔG_{gas}^{assoc}	standard free energy change for association reaction in gas phase. (kJ/mmol)
$\Delta G_{solvent}^{assoc}$	standard free energy change for association reaction in solvent. (kJ/mmol)
ΔG_{es}^{nett}	standard free energy change for solute-solvent electrostatic interaction. (kJ/mmol)

ΔG_{es}^{nett}	standard free energy change for solute-solvent van der Waals interaction. (kJ/mmol)
$\Delta G_{solvent\ effect}^{nett}$	difference in free energy change between reaction in solvent and in gas phase. (kJ/mmol)
ΔH	heat of mixing. (kJ/mmol)
$\frac{\Delta\Delta G}{RT}$	polar free energy parameter (preferential sorption-capillary flow).
I	ionization potential. (V)
J _{ch}	rate of chemical reaction per unit volume.
J _{ent}	rate of entropy change per unit area.
J _i	generalised thermodynamic flux.
J _s	solute flux through membrane. (mmol/cm ² .s)
J _v	total solvent volume flux through membrane. (cm/s)
J _w	water flux through membrane. (cm/s)
k	Boltzman constant.
K	mass transfer coefficient. (cm/s)
K _s	partition coefficient of solute.
K ₁ , K ₂ , K ₃	membrane transport coefficients.
L _p , L _{pD} , L _D	phenomenological coefficients of the linear laws. (cm/s.kPa)
l	Kihara parameter.
N	Avogadro's Number. (molecules/mol)
N _A , N _B	solute flux, solvent flux through membrane. (mmol/cm ² .s; cm/s)
P, ΔP	pressure, operating pressure. (kPa)
Ph	local hydraulic permeability.
ps	solute permeability. (mmol/cm ² .s)
pi	partial pressure. (kPa)
Q	van der Waals variable.
R	membrane rejection coefficient.
R	gas constant, (J/mol.K)

r	correlation coefficient.
R_{\max}	rejection coefficient at infinite volume flux.
$S^*, \Sigma S^*$	modified Small's number.
ΔS	entropy of mixing.(J/mol.K)
T	absolute temperature. (°C)
t	time (s).
TSA, ATSA	total cavity surface area, adjusted TSA.(nm ²).
u_i, u_j	local velocities of components i and j. (cm/s)
V_i	partial molar volume of component i. (nm ³)
Δx	membrane thickness. (nm)
x_i	mole fraction of component i.
γ_i	activity coefficient of component i.
δ_T	total solubility parameter. (J/m ³) ^½
$\delta_h, \delta_p, \delta_n$	partial solubility parameters. (J/m ³) ^½
δ^*	coefficient associated with steric parameter.
Δ	ionization potential. (eV)
ϵ	dielectric constant.
ϵ	solute adsorption constant.
η	viscosity of solution. (Pa.s)
μ	dipole moment, (Debyes)
μ_i	chemical potential of component i.
$\bar{\mu}_i$	electrochemical potential of component i.
$\pi, \Delta\pi$	osmotic pressure, difference in osmotic pressure. (kPa)
ρ	density. (mmol/cm ³)
σ	reflection coefficient.
σ	London parameter, (cm ³)
σ^*	Taft coefficient.
τ	membrane tortuosity coefficient.

(xxvi)

ϕ	coefficient in Eq. 4.114. (mmol/cm ² .s)
Φ	local free energy dissipation function.
ζ	coefficient in Eq. 4.114. (mmol/s)
ω	coefficient of solute permeability.
ω^*	coefficient associated with modified Small's number.
v^*	molar average velocity. (cm/s)

ABBREVIATIONS

COD	chemical oxygen demand (mg/ℓ)
CSIR	Council for Scientific and Industrial Research
DAF	dissolved air flotation
FI	fouling index
MFI	modified fouling index
MMF	multi media filter
NIWR	National Institute for Water Research
NPOX	non-purgeable organic halogens
PI	plugging index
POX	purgeable organic halogens
PS	polysulphone
PWV-area	Pretoria-Witwatersrand-Vereeniging area
RO	reverse osmosis
SDI	silt density index
TDS	total dissolved solids mg/ℓ
THM	trihalomethanes
THMP	trihalomethane formation potential
THMT	terminal trihalomethane value
TOC	total organic carbon
TOHP	total organohalogen formation potential
TOX	total organic halogens
TSA,ATSA	total cavity surface area; adjusted total cavity surface area (nm ²)
UF	ultra filtration
UVA	ultraviolet absorbance
WRC	Water Research Commission

CHAPTER 1

INTRODUCTION

1.1 GENERAL CONSIDERATIONS

Demands on fresh water resources are escalating worldwide as a result of population growth and higher living standards, and growth in industrial, economic and agricultural activities. In many areas economically available fresh water resources are being exploited to their maximum assured yields. South Africa is no exception to this and in some areas shortages have been and are being experienced in spite of augmentation by interbasin water transfer.

Projections of supply and demand indicate that potentially available fresh water resources should be sufficient to meet South Africa's demands until around the year 2020 on a national basis. (Du Plessis and Van Robbroeck, 1978; Bekker and Roberts, (1981); Kriel, 1983). However, due to the uneven distribution of water resources and the recurrence of droughts in South Africa (in particular those of longer duration) it can be expected that water shortages will be experienced periodically in different areas of the country. In order to alleviate these problems large water transfer and water importation schemes will have to be constructed to transfer or import water from areas with surpluses to areas experiencing shortages. Such schemes are highly capital intensive and are in direct competition for public funds with other priority areas of the economy. Shortages in funds could therefore cause delays in the construction of such schemes, aggravating water shortages at times.

In addition to water shortages, increasing water demands present the further problem of deterioration in water quality. Growing water demands and water usage inevitably result in the discharge of increasing volumes of treated sewage and industrial waste waters and other return flows to rivers and dams which are being used as water supply sources. This causes an accumulation of non-degradable substances in the water supply. The only means of arresting or reversing such accumulations would be to import unpolluted fresh water on a large scale to supplement and dilute existing supplies and/or to employ advanced water reclamation processes to remove these substances from the water supply.

1.2

The problems of water shortages and deteriorating water quality are to a large extent interlinked and should, therefore, be addressed as one overall issue in planning strategies. Water reclamation and water reuse are measures which could be implemented to alleviate part of this problem in certain areas and should be considered as elements of an overall planning strategy to make the best use of available water supplies in a particular supply area.

This thesis, therefore, investigates the feasibility of reverse osmosis as a water reclamation process in the context of water supply in South Africa. It focusses, in particular, on the potential applications of reverse osmosis, its economic viability, and the removal of dissolved organic compounds from water by reverse osmosis.

1.2 WATER REUSE

Water reuse takes place in many different ways. The most widely occurring form of reuse is through indirect recycling where treated effluents are discharged to a river and subsequently abstracted by downstream users in admixture with the natural flow of the river. Water reclamation on the other hand has been defined as "the production of water from a wastewater for a particular reuse application" (Water Research Commission, 1982) and implies direct recycling of the reclaimed water, in contrast to indirect recycling.

The term water reclamation includes different concepts i.e. the reclamation of potable water from treated sewage effluents for direct reuse in the municipal supply e.g. Windhoek, South West Africa/Namibia (Van Vuuren et al., 1980); the reclamation of water from treated sewage effluents for direct reuse in a dual supply system, i.e. not for potable use e.g. St Pietersburg Fl. USA (Duynslager, 1979); and the reclamation of water from treated sewage effluents for direct industrial reuse (Giampitri et al., 1978).

1.3

Indirect recycling or indirect reuse usually involves only conventional sewage treatment processes and conventional water treatment processes while a water reclamation plant consists of a series of advanced unit processes. The two systems of reuse will therefore differ with respect to economics and water quality and will be affected differently by local conditions and other factors.

In Chapter 2 the potential role of water reclamation in South Africa is discussed for situations both where indirect reuse occurs and where indirect reuse does not occur. A desk study was conducted to determine potential applications of reverse osmosis in water reclamation applications, the economic feasibility of reverse osmosis as a water reclamation process and the efficacy of reverse osmosis for the removal of different contaminants.

This information was required in order to decide on the further course of action to be followed. The findings indicated that two aspects should be pursued. Firstly, pilot plant studies should be conducted to investigate the practical feasibility of reverse osmosis and to obtain design criteria for larger-scale application. The second aspect that was identified for further study was the removal of dissolved organic compounds by the reverse osmosis process.

1.3 REVERSE OSMOSIS PILOT PLANT STUDIES

In order to obtain information on the practical performance of reverse osmosis in water reclamation applications, a pilot plant study with the following objectives was conducted. The main objectives were to determine pretreatment and membrane cleaning requirements in order to maintain membrane flux at an economically acceptable level. This aspect was identified in the desk study as one of the factors which could significantly affect the economics of the process. Further objectives were to obtain information on expected membrane life and on the quality of reclaimed water that can be produced.

1.4

The results from these studies are summarized and the findings discussed in detail in Chapter 3. Problems which were encountered are considered and possible causes for these problems are discussed. Based on the findings of these studies a recommendation was submitted to the Water Research Commission that a relatively small full-scale reverse osmosis plant be constructed in a practical water reclamation application in order to obtain design and operating criteria for full scale application. This plant (400 m³/d) is scheduled for commissioning towards the end of 1986 to reclaim water that will be used as a boiler feed water in the Port Elizabeth Power Station from purified sewage effluent.

1.4 THE REJECTION OF DISSOLVED ORGANIC COMPOUNDS BY REVERSE OSMOSIS MEMBRANES

One of the primary points of concern in the use of reclaimed water in municipal supplies is the possible presence of harmful dissolved organic compounds in reclaimed water. Reverse osmosis membranes remove higher molecular mass organics very effectively but compounds with a molecular mass of lower than about 150 are removed with varying degrees of efficiency.

In order to be able to predict the rejection of organics of concern in water reclamation applications by reverse osmosis membranes, a detailed literature and experimental study was conducted with the following objectives :

- (a) to review existing membrane models and other correlations that can be used in a simple way to predict the rejection of organics, and to identify or adapt and evaluate those that can be used for this purpose;

1.5

- (b) to identify and quantify factors which affect the removal of organics by reverse osmosis membranes; and
- (c) to generate experimental data that can be used in the evaluation of the models.

These studies are described, and the results and findings are discussed in detail in Chapter 4.

CHAPTER 2

DESK STUDIES ON THE POTENTIAL ROLE AND FEASIBILITY OF REVERSE OSMOSIS FOR WATER RECLAMATION

2.1 INTRODUCTION

As is pointed out in Chapter 1, water reclamation and water reuse are measures that could be implemented to enhance the utilization of available water supplies. However, before embarking on any detailed studies or pilot plant projects on this subject it was necessary to establish whether water reclamation by reverse osmosis is practicable in the South African context. For this reason desk studies were conducted to determine :

- (a) the potential benefits of reverse osmosis in different water reclamation applications, and the potential applications in South Africa; and
- (b) the economic feasibility of reverse osmosis, and
- (c) the efficacy of reverse osmosis for the removal of different contaminants and the quality of reclaimed water that can be produced.

2.2 POTENTIAL APPLICATIONS OF REVERSE OSMOSIS IN SOUTH AFRICA AND POTENTIAL BENEFITS OF REVERSE OSMOSIS

In order to establish the potential role of reverse osmosis and other advanced desalination technologies in the South African water economy, a survey was conducted during 1982/83 to determine potential applications of these technologies in South Africa. The findings from this survey were published in "Desalination - A South African Perspective" (Schutte, 1983).

Potential applications of reverse osmosis (and other desalination technologies) were considered for the desalination of brackish water, the desalination of sea water, the treatment and desalination of industrial and mining effluents, and the reclamation of sewage effluents for direct recycling.

2.2

The findings from this survey are updated and summarized below :

2.2.1 Desalination of brackish water

Although only a small part of South Africa's total water supply is derived from ground water, vast areas in the dry regions of the country rely on ground water for their fresh water requirements. These areas in the dry Western, Central and South-Eastern parts of the country are sparsely inhabited mainly by farming communities, small settlements and towns, and a few major towns such as Beaufort West and Graaff-Reinet. The underground water supplies in these areas are generally fairly brackish with TDS concentrations of more than 1 000 mg/ℓ. In most parts of this region, with average precipitation of less than 300 mm/a and evaporation rates exceeding 1 600 mm/a, surface supplies are small and cannot be relied upon.

The following are small settlements where water supply problems are experienced or expected : Bitterfontein, Brandvlei, Garies, Kamieskroon, Karkams, Nuwerus, Rietpoort, VanWyksvlei, Williston.

In addition to the communities mentioned above, there are numerous farm settlements with populations ranging from a few to a few dozen, some of which also have to rely on rain water collected from roofs for drinking purposes and when rain water is not available they have to use the available brackish water.

From the foregoing it is evident that many small communities have water supply problems which could be alleviated by desalination of available brackish water. It is, however, also true that most of these communities can neither afford the cost of desalination nor do they have or can afford the expertise required to operate and maintain commercially available desalination plants. In order for desalination to be viable in these areas subsidization will be required as well as some form of technical support from a regional body on a regular basis.

2.3

Larger towns in the dry areas of the country which face water supply problems and are in a better position to afford desalination plants are Calvinia, Kenhardt, Port Alfred, Steytlerville, Willowmore, Beaufort West, Graaff-Reinet, De Aar. (Figure 2.5, page 2.25).

Calvinia has a population of about 8 600 and maintains a growth rate of about 2% per annum. It relies on the Karee Dam and local boreholes for its water of reasonably good quality which should be sufficient to supply demands until the end of the century. A number of brackish boreholes are also available at high TDS concentrations. Should the water demand grow faster than the projected 2% per year or if the yield of the other sources should fall, the brackish waters will have to be desalinated to meet the water demand.

Kenhardt with a population of 4 200 has a negative growth rate in its white and a 3% growth rate in its coloured population. The present sources should last for a further two decades. Problems are encountered with a relatively high fluoride content ($\pm 3 \text{ mg}/\ell$) in the water supply. The fluoride level needs to be reduced but this can be done more cheaply than by applying a general, desalination process.

Port Alfred is a small coastal town at the mouth of the Kowie River in the Eastern Cape. It suffers from severe water supply problems since the tidal Kowie River has a TDS concentration of over 2 000 mg/ℓ and the water supply from the Mansfield Dam (in a tributary of the Kowie River) is also about 1 500 mg/ℓ . The present water demand equals the yield of the Mansfield Dam ($0,4 \times 10^6 \text{ m}^3/\text{a}$) and the demand is expected to increase at a steady rate. In addition the town is a popular holiday resort with a peak water demand during the summer holiday period.

The only option to improve the water situation is by desalination of the available brackish water. All of Port Alfred's supplies have a TDS concentration of well over 1 000 mg/ℓ and needs to be desalinated. The present demand is about 1 000 m^3/day which is expected to increase to 3 000 m^3/d by the turn of the century.

2.4

Steytlerville. This small Karoo town with a population of about 3 800 has as its only water source a borehole with a TDS of more than 2 000 mg/ℓ. The present water demand is about 260 m³/d which is expected to rise to about 330 m³/d in the year 2000. Better quality water is available on a farm some distance away from Steytleville. However, desalination of the available brackish water is strongly considered and depending on the economics (power is developed locally at high cost) the potential application of desalination seems good.

Willowmore. The water supply for this Karoo town is derived from a farm about 29 km from town. The total yield is about 700 m³/d which is expected to be adequate to meet the town's water demand until the end of the century when alternative sources such as the desalination of available brackish water will have to be considered.

Beaufort West : The present population of this important Karoo town which has been declared an official growth point, is about 25 000 and maintains a growth rate of about 2,5%. The present water demand of about 4 800 m³/d is being met from the Gamka Dam and a number of boreholes with a total yield of 5 100 m³/d. These sources should be able to meet the demand until the latter half of the 1980's when other underground sources with TDS concentrations of less than 1 000 mg/ℓ are available to be developed. This should meet the demand until the middle of the 1990's. Ideally the TDS concentration in the water supply of a town of this size should not exceed 500 mg/ℓ and if this level is set as a requirement, desalination will have to be introduced to lower present TDS levels. If this is not required then desalination will only have to be introduced towards the end of the century.

Graaff-Reinet is a major Karoo town with a population of about 30 000 and a growth rate of about 2%. The present water supply sources are the Van Ryneveldspas Dam and four local boreholes with a total yield of 16 000 m³/d which should be sufficient to meet the town's water requirements until the late 1990's. There is, however, evidence that the quality of the borehole water is deteriorating and that desalination may have to be introduced at an earlier stage.

2.5

De Aar : The present population of De Aar is about 24 000 with a water demand of roughly $2,7 \times 10^6 \text{ m}^3/\text{a}$. The demand is expected to grow at an annual rate of between 3 and 4% which means that current sources together with known additional sources ($3,8 \times 10^6 \text{ m}^3/\text{a}$) will be able to meet the demand until about 1995. At that stage water reclamation may be an economically viable alternative to importing water from the Orange River which will be the only alternative source of supply.

2.2.2 Sea-water desalination

The largest percentage of world-wide installed desalination capacity is for desalination of sea water. This amounted to 76% of the total installed capacity of about $7,3 \times 10^6 \text{ m}^3/\text{d}$ in 1980 (Techno Economic Services, 1981). However, the cost of sea-water desalination is still markedly higher than the cost to supply water from runoff (Reed 1982). For this reason the large-scale desalination of sea water in South Africa appears to be remote at this stage.

Desalination of sea water can be considered for some small communities on the west coast where water shortages are experienced, viz. Port Nolloth and Hondeklipbaai and where alternative sources are not available.

The first potential large-scale application of sea-water desalination can be expected in the Cape Town area. Present developed water sources have a dependable yield of $268 \times 10^6 \text{ m}^3/\text{a}$ which should meet demand until about 1990. The Palmiet River scheme is expected to supply another $127 \times 10^6 \text{ m}^3/\text{a}$ and meet the demand until about the year 2000 whereafter only smaller sources are available to develop.

At that stage the only alternatives available to augment supplies will be sea-water desalination and water reclamation. Current estimates show that the cost of sea-water desalination is more than twice the cost of water reclamation by reverse osmosis. It appears, therefore, at this stage that large-scale desalination of sea water in the Cape Town area will only materialise well after the turn of the century.

2.6

The East London-King William's Town area is a second potential area where desalination of sea water or water reclamation may be considered after the turn of the century. Development of the Amatole scheme has started in early 1986 and when completed the scheme will supply in the demand of this area until about the year 2000, when water reclamation or sea-water desalination will have to be considered. The Great Kei River is a further potential supply source for this area and its development will, no doubt, be considered in future, which could result in further postponement of any sea-water desalination scheme.

Sea-water desalination in the other major coastal areas i.e. Port Elizabeth and Durban is even less likely since supplies should meet the demand in these areas until beyond 2020.

2.2.3 Treatment and desalination of industrial and mining effluents

Many industrial and mining effluents contain relatively high concentrations of dissolved solids. Current procedures are to dispose of these effluents in evaporation ponds or to discharge them to municipal sewers or the water environment (sometimes after dilution with fresh water). These disposal methods result either in a loss of water, or in contamination of water supplies with dissolved solids or both. The application of desalination processes for the treatment of industrial effluents results in the reclamation of water that can be reused and also prevents the pollution of receiving waters by dissolved solids.

Discharge of effluents is controlled by standards which are from time to time promulgated in terms of the Water Act (Act 45 of 1956). The limits regarding dissolved inorganic solids in effluents are in terms of electrical conductivity. The Special Standard for sensitive catchments stipulates that the conductivity of any discharge is not to be increased by more than 15 per cent above that of

2.7

the intake water. The General Standard for other areas limits the conductivity of effluents to 75 mS/m above that of the intake water. Furthermore, the conductivity of any discharge may not exceed 250 mS/m (equivalent to about 1 750 mg/ℓ total dissolved solids typically). (Government Gazette, 1984).

In order to comply with these standards many industries will have to incorporate desalination processes in their effluent treatment systems. The following gives a brief review of the industries where reverse osmosis could play a role in effluent treatment and desalination.

The mining industry : The sources of mineral pollution arising from mining activities are :

- (i) underground mine waters pumped to the surface and containing relatively high concentrations of dissolved solids, mainly calcium sulphate, iron and manganese;
- (ii) process effluents which can contain very high concentrations of dissolved solids; and
- (iii) runoff from slimes dams and sand dumps which contributes to non-point pollution sources and which has not been quantified.

Pumpage of underground mine waters is a very large point source of mineral pollution to the Vaal Barrage system amounting to about $41 \times 10^6 \text{ m}^3/\text{a}$ on average for the period October 1977 to September 1982, contributing approximately 135 000 tons of dissolved solids on average per annum. (Alexander, 1984). This means that pumpage constitutes only 12% of the point source flow discharged into the Vaal Barrage but it contributes about 40% of the salt load. These figures do not include pumpage from mines outside the catchment of the Vaal Barrage such as the West Rand, the Western Transvaal and Orange Free State gold mines.

2.8

Pumpage from the East Rand mines is at present being discharged to streams draining to the Vaal Barrage, while pumpage from the Orange Free State mines is disposed of by evaporation.

Removal of this point source from the inflow to the Barrage will mean removal of 40% of the point source salt load and will therefore result in a marked improvement in water quality. Since underground mine waters are almost saturated with respect to calcium sulphate, serious scaling problems can be expected when the water is desalinated. For this reason research is being conducted to determine the feasibility of the seeded slurry reverse osmosis process for the desalination of these mine waters. First indications are that the seeded reverse osmosis process holds sufficient promise to warrant further development (Harries, 1985).

Chemical and metallurgical industries : The type of effluent generated by the chemical industry depends on the raw materials being used and the final products. Most industries produce effluent streams generally containing a complex mixture of inorganic and organic dissolved solids, brines from separation processes, regeneration chemicals and waste chemicals.

The concentration of these dissolved materials depends on in-house water management, in-plant treatment and internal recycling. Depending on the nature of the contaminants some effluents may be discharged without treatment to municipal sewers while in other cases, especially those in critical catchments such as the catchment areas of water supply sources, effluents will have to undergo extensive treatment before discharge and still in other cases no discharge of effluents will be allowed. Most smaller industries discharge directly to a municipal sewer and they are subject to the by-laws of the local authority receiving the effluents.

Desalination of the complex types of waters containing process effluents, brines, regenerants etc. has been achieved successfully by means of vapour compression distillation incorporating a seeded slurry system (Anderson, 1979). However, it is necessary to obtain full analyses of any effluent stream to be desalinated and if possible to conduct pilot-scale investigations before a decision is taken on a full-scale plant.

Pulp and paper, textile, hides and skins, food and related industries : Effluents from these industries contain relatively high concentrations of dissolved inorganic solids together with some organic material in dissolved or colloidal form which may cause fouling in desalination plants. Tubular ultrafiltration and reverse osmosis have proved successful in the treatment of some of these effluents. (Hart and Squires, 1985).

Only limited work has been done in this area and initial research done by the University of Natal on the treatment and desalination of effluents containing high concentrations of inorganic and organic materials has resulted in follow-up studies in the pulp and paper industry and in treatment of abattoir wastes (Buckley, 1985).

In some cases products may be recovered so that it becomes economically attractive to treat these effluents from the point of view that water as well as products may be recovered.

It can be expected that many of the larger industries in this group especially those in sensitive catchments will be forced to consider desalination of their high TDS effluents.

The power generating industry : The main source of effluent from power stations is cooling water blow-down and brines and regenerants from the preparation of boiler feed water. The volume of effluent depends on the installed capacity of the power station, the quality of feed water and possible consumptive use of the effluents in the ashing system. A 3 600 MW station receiving water of about 200 mg/l TDS can produce up to 10 Ml/d of effluent which has to be disposed of.

Desalination of these effluents can be done successfully with seeded slurry vapour compression distillation (Anderson, 1979) which will produce a high quality product water and a crystallised brine. Electrodialyses reversal and tubular reverse osmosis have proved on pilot-scale to be able to desalinate cooling water blow-down, producing water which can be recycled and a brine of about 10-15% of the blow-down. At present two full-scale plants are under construction to treat cooling water blow-down : An electrodialysis reversal plant at the Tutuka Power Station and a tubular reverse osmosis plant at the Lethabo Power Station (Spencer, 1985).

2.2.4 Water reclamation from sewage effluents

As is discussed in Chapter 1 water reuse can take place either through water reclamation and direct reuse or through the indirect reuse of purified sewage effluents which are discharged to rivers and water bodies which are being used as a source of raw water. Diagrammatically, the two systems can be presented as shown in Figure 2.1. Indirect reuse occurs widely in South Africa with the water supply and reuse system in the Pretoria-Witwatersrand-Vereeniging (PWV) area a prime example. Figure 2.2 gives a diagrammatic simplified representation of this system showing the different indirect reuse sub-systems.

In this discussion concentration of total dissolved solids (TDS) and total organic carbon (TOC) will be considered.

In order to demonstrate the differences between indirect reuse and water reclamation and direct reuse the simple systems as shown in Figure 2.1 will be used. Basically the different reuse systems in the PWV area are similar to the system described in Figure 2.1(b); the main difference being that effluent from one area is reused in another area and furthermore, that effluent from one area is subsequently reused more than once in different areas as shown in Figure 2.2.

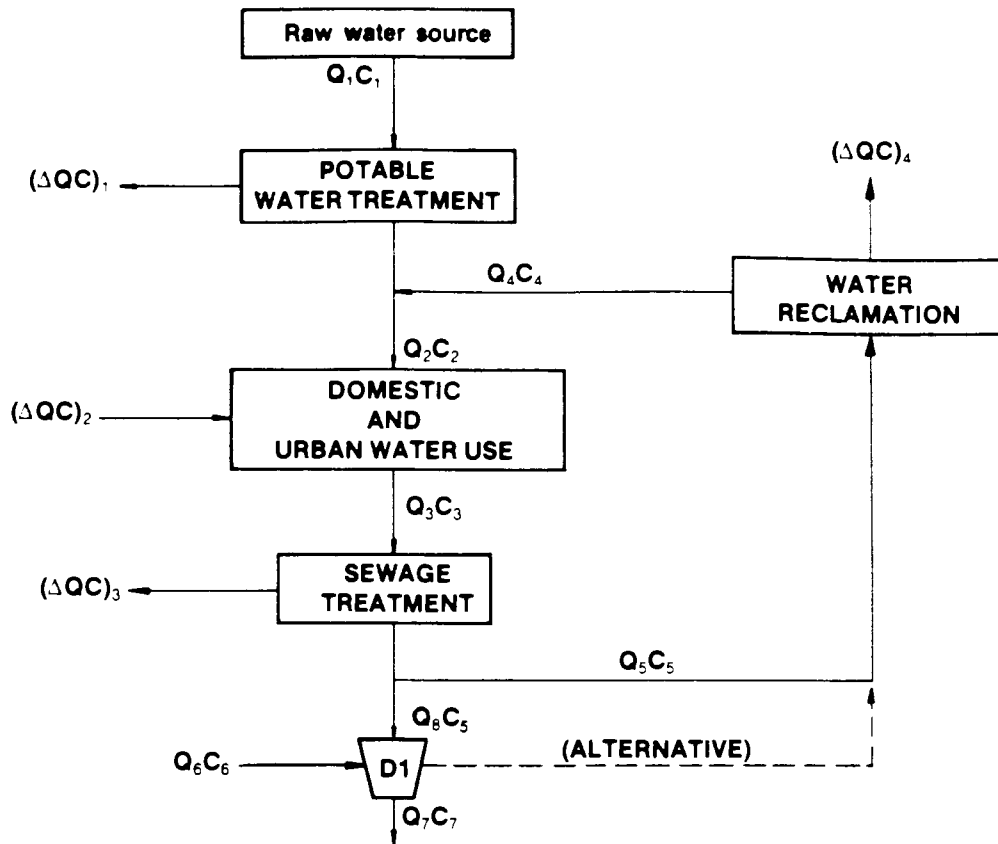


FIGURE 2.1(a): SCHEMATIC REPRESENTATION OF A SYSTEM FOR WATER RECLAMATION AND DIRECT RE-USE

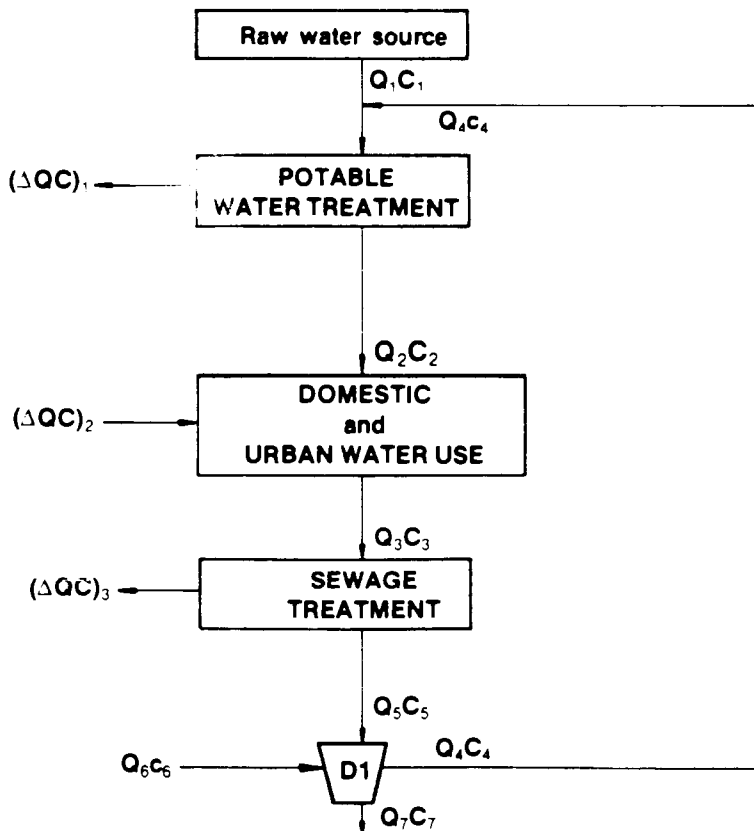


FIGURE 2.1(b): SCHEMATIC REPRESENTATION OF A SYSTEM FOR INDIRECT WATER RE-USE

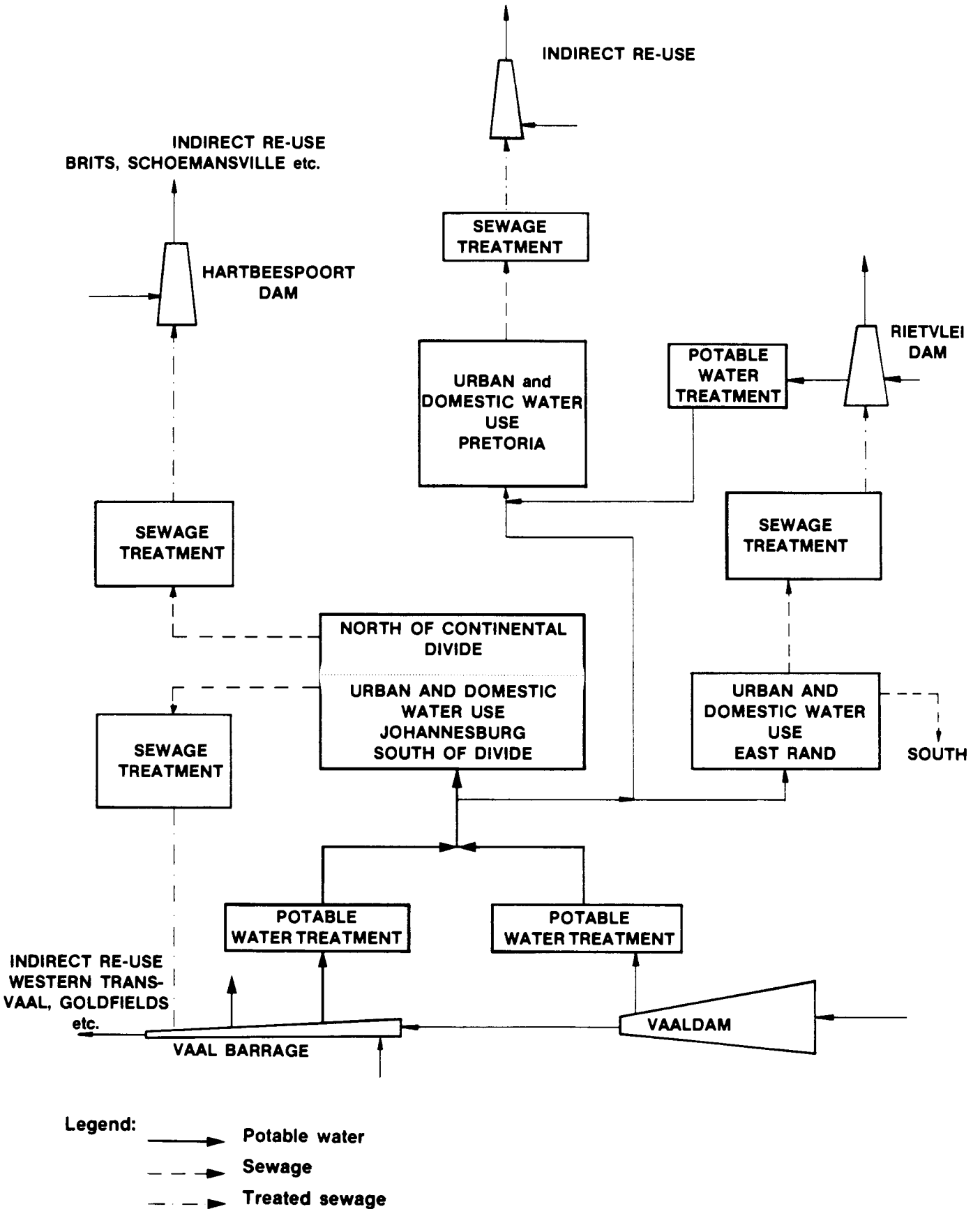


FIGURE 2.2: SIMPLIFIED DIAGRAMMATIC REPRESENTATION OF WATER RE-USE IN THE PRETORIA—WITWATERSRAND—VEREENIGING AREA

A mass balance for any constituent in the water can be drawn up as follows for the indirect system in Figure 2.1(b) :

$$Q_1C_1 + Q_4C_4 - (\Delta QC)_1 = Q_2C_2 \quad \dots\dots\dots 2.1$$

$$Q_2C_2 + (\Delta QC)_2 = Q_3C_3 \quad \dots\dots\dots 2.2$$

$$Q_5C_5 + Q_6C_6 = Q_4C_4 + Q_7C_7 \quad \dots\dots\dots 2.3$$

$$Q_3C_3 - (\Delta QC)_3 = Q_5C_5 \quad \dots\dots\dots 2.4$$

The concentration of any substance or group of substances in the potable water supply, i.e. C_2 is of importance and is given by :

$$C_2 = \frac{Q_1C_1}{Q_2} + \frac{Q_4C_4}{Q_2} - \frac{(\Delta QC)_1}{Q_2} \quad \dots\dots\dots 2.5$$

$$= \frac{Q_1C_1}{Q_2} + \frac{Q_4}{Q_2} \left[\frac{Q_5C_5 + Q_6C_6 - Q_7C_7}{Q_4} \right] - \frac{(\Delta QC)_1}{Q_2} \quad \dots\dots\dots 2.6$$

$$= \frac{Q_1C_1}{Q_2} + \frac{Q_5C_5 + Q_6C_6 - Q_7C_7}{Q_2} - \frac{(\Delta QC)_1}{Q_2} \quad \dots\dots\dots 2.7$$

$$= \frac{1}{Q_2} \left[Q_1C_1 + Q_5C_5 + Q_6C_6 - Q_7C_7 - (\Delta QC)_1 \right] \quad \dots\dots\dots 2.8$$

$$= \frac{1}{Q_2} \left[Q_1C_1 + Q_3C_3 - (\Delta QC)_3 + Q_6C_6 - Q_7C_7 - (\Delta QC)_1 \right] \quad \dots\dots\dots 2.9$$

A mass balance for any constituent in the water for the direct reuse system with water reclamation (Figure 2.1(a)) is as follows :

$$Q_1C_1 + Q_4C_4 - (\Delta QC)_1 = Q_2C_2 \quad \dots\dots\dots 2.10$$

$$Q_2C_2 + (\Delta QC)_2 = Q_3C_3 \quad \dots\dots\dots 2.11$$

$$Q_3C_3 - (\Delta QC)_3 = Q_5C_5 \quad \dots\dots\dots 2.12$$

$$Q_4C_4 = Q_5C_5 - (\Delta QC)_4 \quad \dots\dots\dots 2.13$$

In this case the concentration of any constituent in the domestic water supply is :

$$C_2 = \frac{Q_1C_1}{Q_2} + \frac{Q_4C_4}{Q_2} \quad \dots\dots\dots 2.14$$

$$= \frac{Q_1C_1}{Q_2} + \frac{Q_4}{Q_2} \left[\frac{Q_5C_5 - (\Delta QC)_4}{Q_4} \right] \quad \dots\dots\dots 2.15$$

$$= \frac{Q_1C_1 + Q_3C_3 - (\Delta QC)_3 - (\Delta QC)_4}{Q_2} \quad \dots\dots\dots 2.16$$

2.14

The two systems will perform identically when

$$(Q_2C_2)_D = (Q_2C_2)_I \dots\dots\dots 2.17$$

where D refers to the direct reuse system and I to the indirect reuse system.

If the volume to be supplied is fixed, i.e.

$$(Q_2)_D = (Q_2)_I \text{ then } \dots\dots\dots 2.18$$

$$(C_2)_D = (C_2)_I \dots\dots\dots 2.19$$

and from 2.9 and 2.16.

$$(\Delta QC)_3,D + (\Delta QC)_4,D = (\Delta QC)_3,I + (\Delta QC)_1,D - (Q_6C_6 - Q_7C_7)_I \dots 2.20$$

For the two systems to perform equally with respect to a particular constituent, the total mass removed by the processes in the direct system must equal the mass removed by the processes in the indirect system, plus the dilution effect or dissipation effect of the dam, viz. $(Q_6C_6 - Q_7C_7)$.

The requirements for equal performance can be demonstrated by the following examples :

EXAMPLE 1

The objective is to produce water with total dissolved solids (TDS) concentration not exceeding 500 mg/l, i.e. $C_2 \leq 500$ mg/l TDS, under the following conditions :

fresh water intake $C_1 = 100$ to 450 mg/l TDS

TDS increase during use cycle $\Delta C_2 = 350$ mg/l TDS

No TDS removal during water treatment and waste-water treatment

$$\Delta C_1 = \Delta C_3 = 0$$

TDS removal by reverse osmosis water reclamation

$$\Delta C_4 = 0,9 \times C_5$$

$$C_4 = 0,1 C_5$$

(i) Indirect reuse system (Figure 2.1(b))

Not considering any dilution, i.e. $Q_6C_6 = Q_7C_7$

$$\begin{aligned} Q_2C_2 &= Q_1C_1 + Q_4C_4 \quad \text{but} \quad C_4 = C_2 + \Delta C_2 \\ &= Q_1C_1 + Q_4(C_2 + \Delta C_2) \end{aligned}$$

$$Q_2 C_2 - Q_4 C_2 = Q_1 C_1 + Q_4 \Delta C_2$$

$$C_2(Q_2 - Q_4) = Q_1 C_1 + Q_4 \Delta C_2$$

and $Q_2 = Q_1 + Q_4$ ($\Delta Q_1 = \text{negligible}$)

$$C_2 = C_1 + \frac{Q_4}{Q_1} (\Delta C_2)$$

The maximum recycle rates that are possible with feed water of different qualities and not exceeding 500 mg/ℓ TDS in C_2 are shown in Table 2.1.

TABLE 2.1 MAXIMUM RECYCLE RATES WITH FEED WATER OF DIFFERENT QUALITIES AND NOT EXCEEDING 500 mg/ℓ TDS IN THE FINAL WATER

Raw water quality C_1 mg/ℓ TDS	Maximum recycle ratio ratio $\frac{Q_4}{Q_1}$
10	1,40
100	1,14
200	0,86
300	0,57
400	0,29
450	0,14
490	0,03

The effect of dilution or pollution of dam D_1 by runoff or discharges, i.e. the effect of $Q_6 C_6 - Q_7 C_7$ will be reflected by changes in C_4 .

$$Q_4 C_4 = Q_5 C_5 + (Q_6 C_6 - Q_7 C_7)$$

$$Q_4 C_4 = Q_5 (C_2 + \Delta C_2) + (Q_6 C_6 - Q_7 C_7)$$

but $C_4 = C_7$

$$C_4 (Q_4 + Q_7) = Q_5 (C_2 + \Delta C_2) + Q_6 C_6$$

$$C_4 = \frac{Q_5}{Q_5 + Q_6} (C_2 + \Delta C_2) + \frac{Q_6}{Q_5 + Q_6} C_6$$

since $(Q_4 + Q_7) = (Q_5 + Q_6)$

If $Q_6 \gg Q_4$, C_4 will be mainly determined by C_6 and if $C_6 \ll 500$ mg/l a high Q_4/Q_1 recycle ratio can be maintained without deterioration in C_2 .

However, if $C_6 > 500$ mg/l (as is the case for example for inflow into the Vaal Barrage under certain conditions) the recycle ratio of Q_4/Q_1 will have to be reduced in order to maintain C_2 values below 500 mg/l.

(ii) Reclamation and direct reuse (Figure 2.1 (a))

When water is reclaimed by reverse osmosis, TDS is removed in the process $(\Delta QC)_4$.

$$\begin{aligned} C_2 &= \frac{Q_1 C_1}{Q_2} + \frac{Q_4 C_4}{Q_2} \\ &= \frac{Q_1 C_1}{Q_2} + \frac{Q_4}{Q_2} (0,1 \times C_5) \end{aligned}$$

In this case C_2 will therefore be lower than 500 mg/l as long as C_1 remains below 500 mg/l. If C_1 is higher than 500 mg/l the reclaimed water will actually dilute the incoming water and the following recycle rates will be needed to maintain C_2 below 500 mg/l.

$$C_2 = \frac{Q_1}{Q_2} (C_1) + \frac{Q_4}{Q_2} (0,1) C_5$$

$$\text{Since, } \frac{Q_1}{Q_2} + \frac{Q_4}{Q_2} = 1$$

$$C_2 = \frac{(1-Q_4)}{Q_2} C_1 + \frac{Q_4}{Q_2} (0,1) C_5$$

$$C_2 - C_1 = - \frac{Q_4}{Q_2} C_1 + (0,1) \frac{Q_4}{Q_2} C_5$$

$$\frac{Q_4}{Q_2} = \frac{C_2 - C_1}{0,1 C_5 - C_1}$$

TABLE 2.2 REQUIRED RECYCLE RATES TO MAINTAIN $C_2 = 500 \text{ mg}/\ell$

Raw water quality TDS mg/ ℓ	Required recycle rate $\frac{Q_4}{Q_2}$
500	0
600	0,20
800	0,44
1 000	0,58
1 200	0,67

EXAMPLE 2

The objective in this example is to produce water with a total organic carbon content (TOC) not exceeding a predetermined value. In the indirect system the TOC concentration in the drinking water is C_2 from Equation 2.10.

$$C_2 = \frac{1}{Q_2} \left[Q_1 C_1 + Q_3 C_3 - (\Delta QC)_3 + Q_6 C_6 - Q_7 C_7 - (\Delta QC)_1 \right]$$

The TOC concentration in the municipal supply in this case is determined by :

fixed factors C_1 and C_3 , and

variable factors $(\Delta QC)_3$, $(\Delta QC)_1$ and $(Q_6 C_6 - Q_7 C_7)$

i.e. the efficacy of the sewage treatment process, the efficacy of the water treatment process, and dilution or pollution from runoff and discharges to dam D_1 .

The efficacy of the treatment processes to remove TOC can be improved by optimizing conventional processes, but this would only have a marginal effect on C_2 . In order to achieve a significant TOC removal an advanced treatment process such as activated carbon adsorption or reverse osmosis must be incorporated in the system. Such a process can be introduced as part of the drinking water treatment process thereby reducing C_2 directly, or as advanced waste water treatment process to reduce C_5 . This latter option will only be viable if dam D_1 is relatively unpolluted i.e. $C_4 \leq C_5$.

If D_1 is polluted, $C_7 \geq C_5$, an alternative to employing advanced drinking water treatment in the indirect system is to introduce water reclamation and direct recycling of reclaimed water. The TOC in the municipal supply, C_2 , in this case is from Equation 2.16 :

$$C_2 = \frac{1}{Q_2} \left[Q_1 C_1 + Q_3 C_3 - (\Delta QC)_3 - (\Delta QC)_4 \right] \text{ and is determined by}$$

fixed factors C_1 and C_3 and variable factors $(\Delta QC)_3$ and $(\Delta QC)_4$.

If $(\Delta QC)_3$ is the same for both the indirect system and for the water reclamation system, we have :

$$(\Delta QC)_{1,D} + (\Delta QC)_{4,D} = (\Delta QC)_{1,I} + (Q_6 C_6 - Q_7 C_7)$$

assuming $(Q_4 C_4)_D = (Q_4 C_4)_I$

where D indicates direct reuse and

I indicates indirect reuse.

If $(\Delta QC)_{1,D} = (\Delta QC)_{1,I}$

the two systems will perform equally, i.e. $C_{2,D} = C_{2,I}$

when $(\Delta QC)_{4,D} = (Q_6 C_6 - Q_7 C_7)_I$

i.e. when dilution provided by unpolluted runoff is equivalent to the TOC load removed by water reclamation.

If $(Q_6 C_6 - Q_7 C_7)_I$ is insufficient to produce an acceptable $C_{2,I}$ then $(\Delta QC)_{1,I}$ must be increased by incorporating advanced processes specifically for TOC removal.

In such a case the decision on which system to employ should be based on economics. For example, if advanced treatment is required for $(Q_1 + Q_4)_I$ where $Q_4 \ll Q_1$ in the indirect case, compared to $(Q_5)_D$ in water reclamation, where $(Q_5)_D = 1/R (Q_4)_D$, with R = recovery factor, water reclamation would appear to be the cheaper alternative. On the other hand, when $Q_4 \ll Q_1$ an acceptable C_2 may be produced without advanced treatment when $C_1 < C_2$, so that the indirect system will be cheaper in this case (although the direct system will produce a better quality water).

In summary the potential role of water reclamation in a particular situation is determined by the following factors :

- (i) The quality requirements for the water supply, C_2 . If quality requirements are lenient, and no standards are set for parameters such as TDS and TOC, indirect reuse of effluents (Figure 2.1(b)) will always be cheaper than water reclamation and direct reuse, (Figure 2.1(a)). This applies to the present South African situation with a TDS recommended limit (500 mg/l) but no TOC limit in effect. As a result indirect reuse (without advanced processes) is used widely.
- (ii) The quality of the water sources, C_1 and C_7 . When C_7 is poorer than C_5 water reclamation will always be the preferred reuse route from a quality, C_2 , point of view. If C_7 is better than C_5 , advanced waste-water treatment is required to prevent pollution of C_7 . If C_7 is poorer than the required C_2 , advanced treatment of Q_4C_4 is required.
- (iii) The required recycle rate $\frac{Q_4}{\hat{Q}_2}$:

If existing $Q_4 = 0$, i.e. no reuse, employment of either system will result in enhanced utilization of Q_1 .

If the required $\frac{Q_4}{\hat{Q}_2} < \frac{Q_1}{Q_2}$ indirect reuse should produce an acceptable $(C_2)_I$ if $(C_1)_I < (C_2)_I$. If the required $\frac{Q_4}{\hat{Q}_2} \geq \frac{Q_1}{Q_2}$ a nett removal of pollutants is required either through $(\Delta QC)_4$ or increased $(\Delta QC)_{1,I}$ or by $(Q_6C_6 - Q_7C_7)$. The cheapest solution producing the required C_2 must be determined for each particular case.

2.2.4.1 Potential applications of water reclamation in South Africa

In a few areas in South Africa indirect reuse of purified effluents does not occur. These areas are generally in the upper catchments of rivers, in relatively isolated areas and in coastal areas where purified effluents are discharged to sea after one use cycle. In these areas the implementation of water reclamation or indirect water reuse will result in improved utilization of available supplies.

The reclamation of sewage effluents for reuse could potentially play a role in many of the relatively small towns in the dry parts of the country. However, the stringent operation, control and surveillance requirements associated with water reclamation will preclude many of these potential applications.

Four areas have been identified where water reclamation could potentially be implemented viz. : (Figure 2.5, page 2.25).

Pietersburg where water supply problems are expected towards the middle of the 1990's. The population in the Pietersburg area of 57 000 in 1980 is expected to increase to more than 300 000 in the year 2020. At this growth rate the available supplies of $41,8 \times 10^6 \text{m}^3/\text{a}$ should meet demands up to about 1994. Since there are no other readily and economically available sources in that area water reclamation seems to be the only feasible alternative.

Possible importation of water from the Olifants or Letaba catchments will be very costly and will have to be considered on a priority basis with other demands on these sources.

East London–King William's Town : The border area has a high priority for development in terms of the National Physical Development Plan and the present population of about 350 000 is expected to double in the next 25 years. The present water sources have a dependable yield of $53 \times 10^6 \text{m}^3/\text{a}$ and should meet the demand until about 1990 when the Amatole scheme which is currently under construction will increase the yield by $36 \times 10^6 \text{m}^3/\text{a}$. This should meet demands until about the year 2000.

At that stage water reclamation will have to be considered as an alternative to sea-water desalination to meet increased demands.

Cape Town : As discussed in Section 2.2.2 present and future sources should meet the water demand of the Greater Cape Town area until about the year 2000 whereafter water reclamation and sea-water desalination are the only other large-scale alternative sources.

The potential role of water reclamation in the water supply of the Cape Town area has been discussed in detail by Schutte and Beekman (1982). A copy of this paper is included as Appendix C1.

Pretoria–Witwatersrand–Vereeniging (PWV) area and Vaal River downstream of Vaal Barrage :

Figure 2.2 shows a simplified diagrammatic representation of the water supply and waste water treatment systems in this area. Due to increasing water reuse and increasing TDS loads in return flows from industry and mines and from runoff, the TDS concentration in the Vaal Barrage water has increased slowly but steadily over the period 1940–1965 and has increased dramatically since then as shown in Figure 2.3 (Alexander, 1984). Table 2.3 gives an indication of the situation in the part of the PWV-area draining to the Vaal River (south of the continental divide).

TABLE 2.3 WATER SUPPLIED AND EFFLUENT DISCHARGE BY DIFFERENT SECTORS IN THE PWV-AREA (1981)

	<u>Municipalities</u>	<u>Industry</u>	<u>Mines</u>	<u>Total</u>
Water supplied to ($10^6\text{m}^3/\text{a}$)	329	117	75	521
Effluent discharged by ($10^6\text{m}^3/\text{a}$)	241	54	41	336
Percentage returned	73	46	55	64
TDS load discharged (t/a)	143 600	65 800	134 600	343 600
Mean effluent concentration (mg/l TDS)	600	1 220	3 270	1 020

The water supply situation downstream from the Vaal Barrage to Parys, Klerksdorp, Orkney and the area served by the OFS Goldfields Water Board is even worse as is shown in Figure 2.4 (Alexander, 1984).

The following options are available to (partly) satisfy the growth in demand and to improve the quality of some existing supplies.

- (i) Importation of good quality water to the region (increased Q_1C_1 in Figure 2.1). This will be achieved by the Usutu-Vaal scheme which will meet the increased demand until about 1995, and the proposed Lesotho-Highlands scheme which will meet the demand until about 2010.
- (ii) Increased reuse rates Q_4/Q_2 in Figure 2.1 which will require nett removal of contaminants by advanced processes and/or water reclamation.

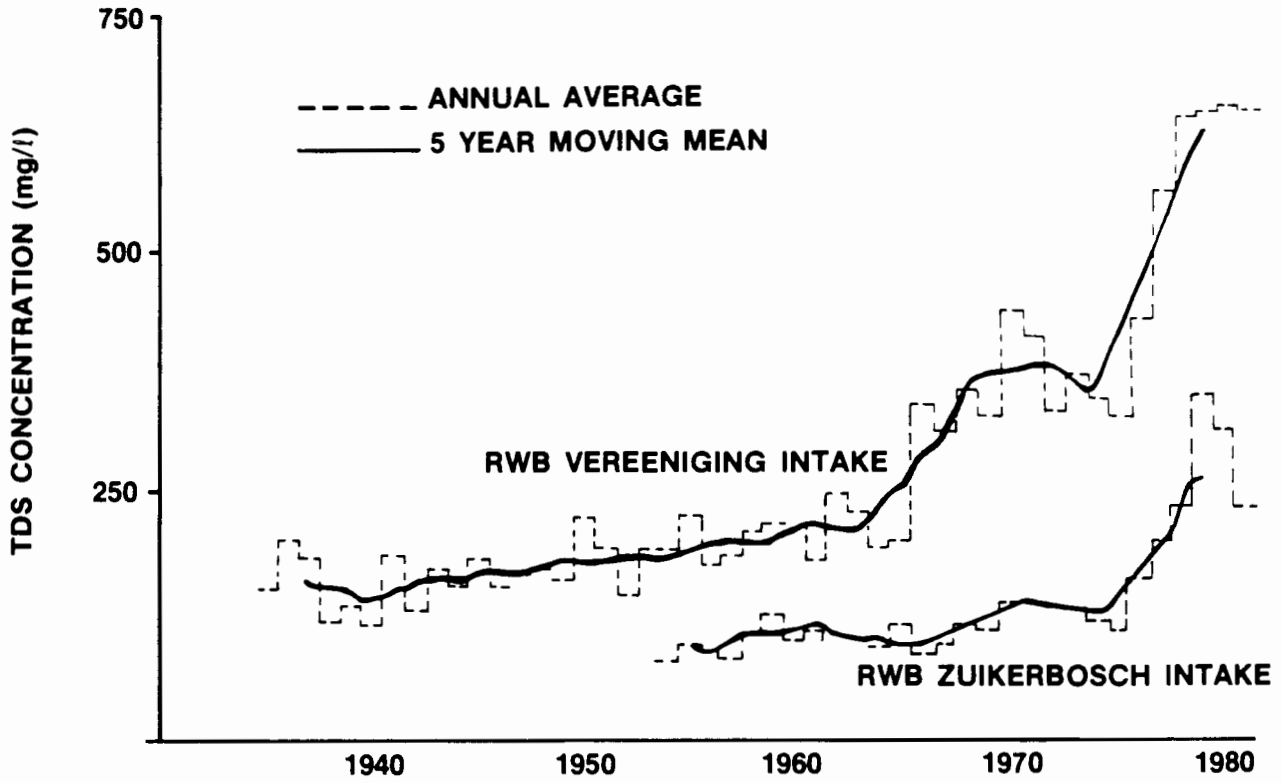


FIGURE 2.3: INCREASE IN T.D.S. CONCENTRATION IN THE VAAL BARRAGE

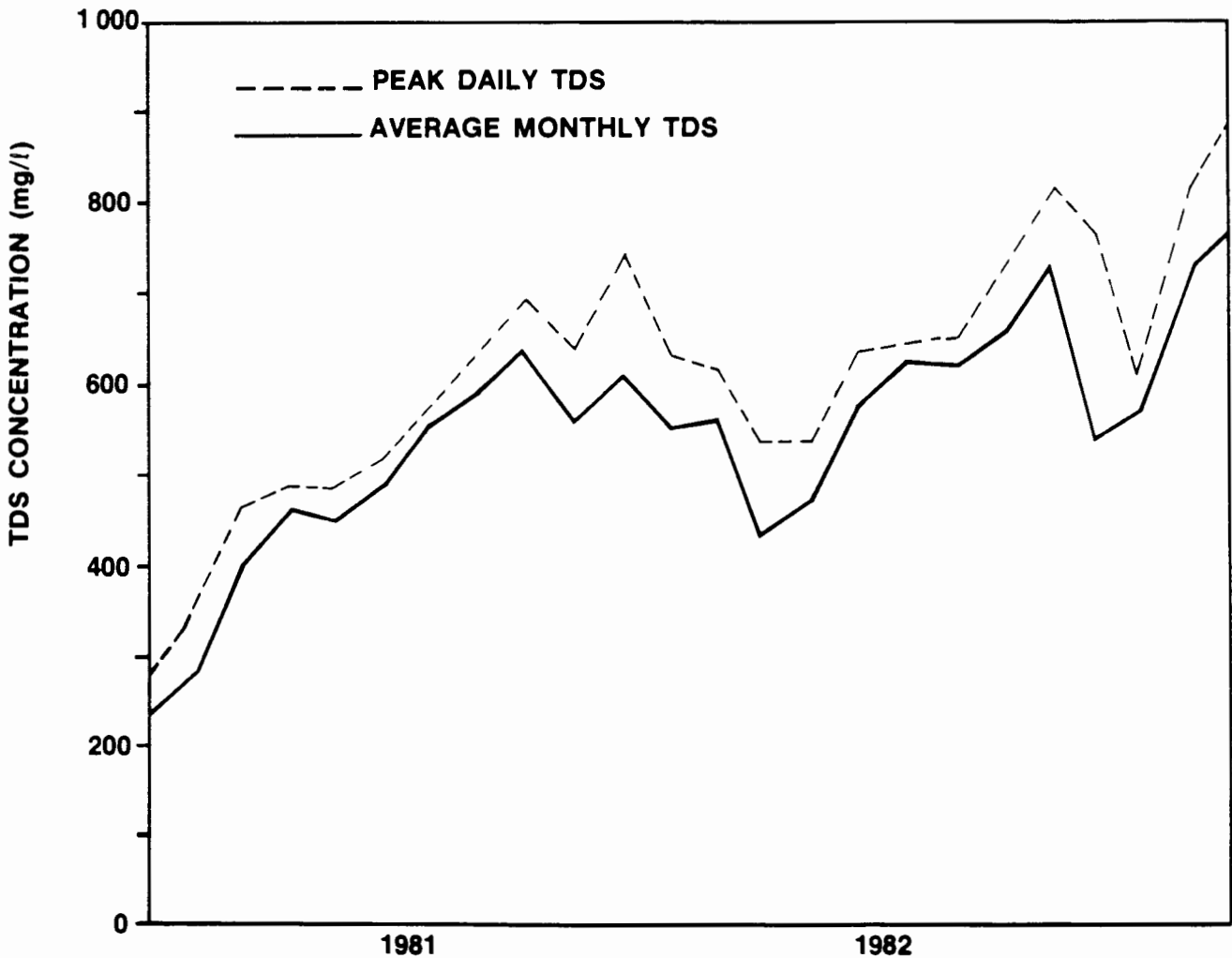


FIGURE 2.4: INCREASE IN T.D.S. CONCENTRATION IN THE VAAL RIVER DOWNSTREAM OF THE BARRAGE

- (iii) Reduction of contaminant loads from inflows to the Barrage (Q_6C_6). As is indicated in Table 2.3 TDS discharges in mine water contribute significantly to the TDS load to the Barrage. Desalination of these effluents as well as certain industrial effluents will contribute to a reduction in TDS in the Barrage (C_6).
- (iv) In the area downstream from the Barrage the only option available is to employ advanced water treatment processes (ΔQC)₁ if the quality of Vaal River water C_1 cannot be improved.

2.2.5 Conclusions

A potential role for reverse osmosis has been shown to exist in different applications, mainly for the desalination of brackish water and for water reclamation applications in industry. Furthermore, a number of potential large-scale applications have been identified where reverse osmosis could be employed to improve the existing water supply situation.

Brackish water desalination by reverse osmosis is a well proven and established process and no further research in this area is currently necessary. However, a number of issues need to be resolved in the application of reverse osmosis in water reclamation applications, including the efficacy of the process to remove contaminants to acceptable levels, as well as the economic viability of reverse osmosis in water reclamation applications. In Sections 2.3 and 2.4 a literature review and desk study on these two aspects are presented.

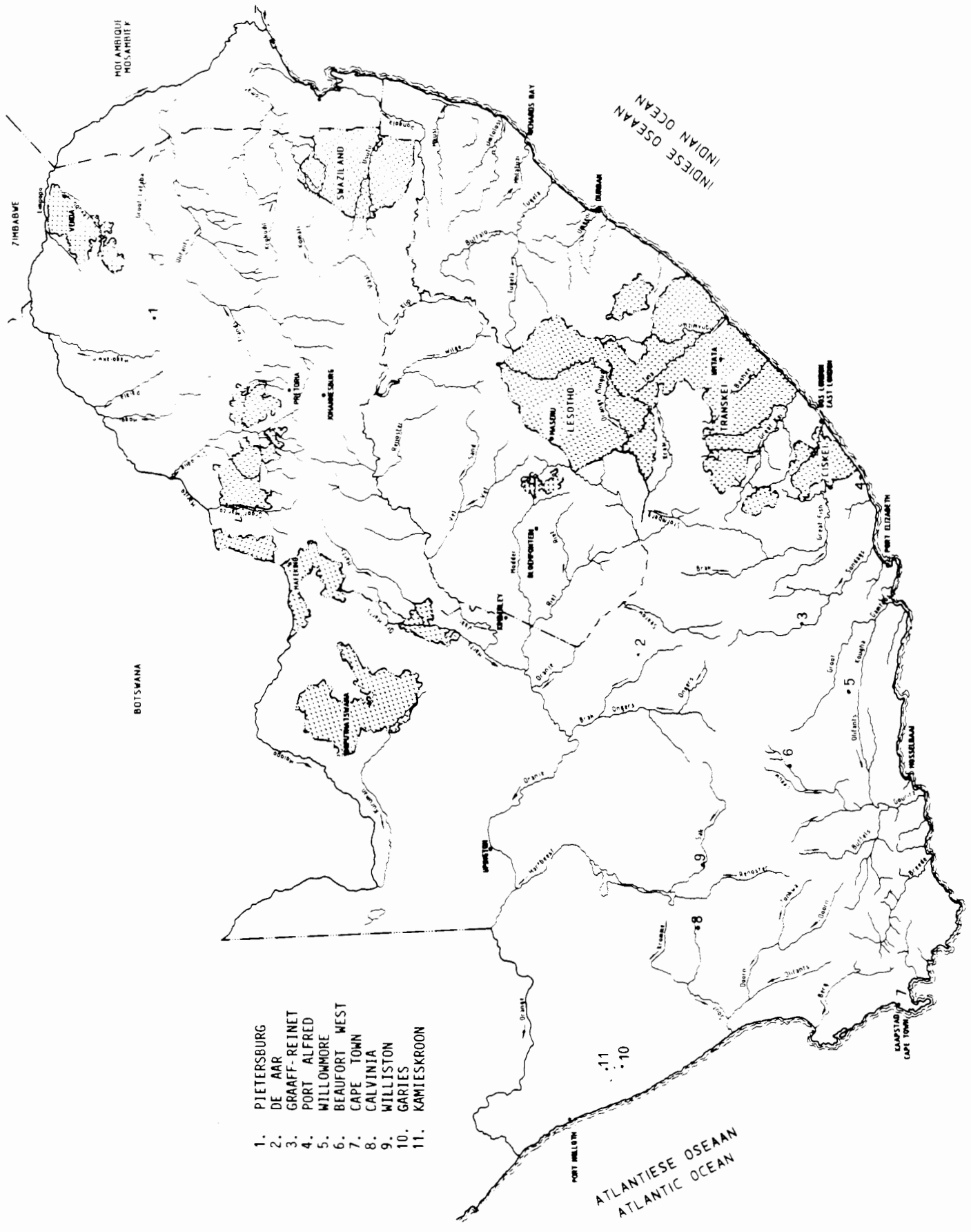


FIGURE 2.5 LOCATIONS WITH POTENTIAL REVERSE OSMOSIS APPLICATIONS

2.3 DESK STUDY ON THE ECONOMIC VIABILITY OF REVERSE OSMOSIS AS A WATER RECLAMATION PROCESS

This study was conducted in order to determine whether the estimated cost of water reclaimed by reverse osmosis is within the range where it could be considered a viable option to augment supplies.

The unit cost for water reclaimed by reverse osmosis (or any other reclamation process) depends on many factors which may be different for different localities and different sites and which will be affected by interest rates, the rate of inflation, exchange rates, the cost of power, availability of services and infrastructure, plant size and many other factors. So, in addition to doing a cost estimate for a particular set of circumstances the effects of variations in the major cost factors on the unit price of the final reclaimed water are also discussed.

The cost items included in the following calculations are those proposed by the International Desalination and Environmental Association (USAID, 1980). The following cost estimate is for the reclamation of 25 000 m³/d water from sand filtered activated sludge effluent with a locally available tubular reverse osmosis plant. Costs are for the last quarter of 1985.

2.3.1 Capital costs

The major direct capital cost for a desalination plant is the desalination equipment, in this case the reverse osmosis plant. However, since the membranes in a reverse osmosis plant have a limited lifetime, usually estimated at 3 years, compared to a plant lifetime of 15 or 20 years, membrane replacement costs are considered an operation and maintenance cost item.

Direct capital costs

- (i) The direct capital cost for a 25 Mℓ/d tubular reverse osmosis plant (excluding membranes) will be in the range of R11 million to R15 million. To this figure must be added other direct capital costs as well as indirect capital costs :

Other direct capital costs :

- (ii) Feed water supply development. This will depend on the locality of the water reclamation plant relative to the waste-water treatment plant (feed supply source) and may involve lift pumps and pipelines.
- (iii) Feed water pretreatment : In tubular reverse osmosis applications this item may involve only sand filtration which can be part of the waste-water treatment plant. In some applications more elaborate pretreatment may be required which may require capital equipment for chemical dosing, clarification, flocculation, sand filtration and disinfection. Acid dosing for pH control and cartridge filtration are always required for cellulose acetate membranes.
- (iv) Site development and cost of a building must be included. An acceptable figure for this is 2% of equipment costs. (USAID, 1980)
- (v) Energy source development and electrical equipment (switch gear) may constitute capital costs of about 2% of desalination equipment capital. (USAID 1980)
- (vi) Brine disposal : In coastal areas this will be limited to pipeline costs for a sea outfall while in inland areas the cost of land for evaporation ponds may be the major capital requirement. If further treatment is required such as evaporation and crystallization, capital costs for a plant to treat 15 to 30% of the feedwater as brine will be required. A plant producing 25 000 m³/d at 80% water recovery with a feedwater flow rate of 31 250 m³/d will produce 6 250 m³/d of concentrated brine.

2.28

A suitable evaporator to treat this volume will cost in the region of R3 million to R5 million. Final disposal from the concentrator is assumed to be in lined ponds. The volume will be $6\ 250 \times 0,05 = 313\ \text{m}^3/\text{d}$ assuming 95% recovery in the evaporator. At a nett average evaporation rate of 6 mm/d a total area of 5,2 ha will be required for final brine disposal.

- (viii) Product water treatment will constitute degassing and final disinfection of the reclaimed water and pipelines and reservoirs for storage. Final activated carbon polishing may be required as a second barrier against organic compounds. However, for this exercise no provision is made for activated carbon adsorption.

Total capital costs for a 25 M ℓ /d plant can be summarized as follows taking the reverse osmosis equipment cost at R12,5 million and the brine concentrator at R4 million.

Figure 2.6 shows the effect of variations in reverse osmosis plant costs in the region of R8 to 13×10^6 on unit water costs.

Direct capital costs

(i)	Reverse osmosis equipment	12 500 000
(ii)	Feed water supply development	100 000
(iii)	Pretreatment	500 000
(iv)	Building	250 000
(v)	Electrical switchgear	250 000
(vi)	Brine concentrator	4 000 000
(vii)	Brine evaporation ponds	100 000
(viii)	Product water treatment	<u>500 000</u>
	Sub-total	<u>18 200 000</u>

2.29

Indirect capital costs

(i)	Interest during construction :	
	15% of direct capital cost for 6 months	1 365 000
(ii)	Project Management fees (2%)	364 000
(iii)	Contingencies (5%)	910 000
(iv)	Start-up costs (2,5%)	<u>455 000</u>
	Sub-Total	<u>3 094 000</u>

Other capital costs

(i)	Land : not considered	-
(ii)	Working capital (2,5%)	<u>455 000</u>
	Sub-Total	<u>455 000</u>

Total capital costs

Total of all capital costs : 21 749 000

Installed capacity unit capital cost : R/m ³ .d	<u>916</u>
Installed capacity unit capital cost based on direct capital costs : R/m ³ .d	<u>728</u>
Based on desalination equipment costs : R/m ³ .d	<u>500</u>

2.3.2 Annual costs

Recurring costs

- (i) Taxes not considered
- (ii) Insurance not considered

(iii) Operation and maintenance costs

(a) Salaries :

1 Plant superintendent	35 000
1 Plant chemist	25 000
1 Chief operator	30 000
5 Senior operators	75 000
10 Assistant operators	<u>50 000</u>
	<u>R215 000</u>

2.30

(b)	General overheads (25% of (a))	55 000
(c)	Membrane replacement : 3 year lifetime and R5 000 000 per full set of membranes	1 667 000
(d)	<u>Energy RO</u> electrical power : R0,05/kW.h specific energy consumption : 2,755 kW.h/m ³ plant factor : 0,9; Annual production : 25 000x365x0,9 = 8 213 000 m ³ /a	1 129 000
	<u>Energy evaporator</u> electrical power : R0,05/kW.h specific energy consumption : 20 kW.h/m ³ plant factor : 0,9; water recovery : 0,95 annual production 6 250x0,9x0,95x365 = 1 950 000 m ³	1 950 000
(e)	Chemicals : Pretreatment, membrane cleaning and disinfection	200 000
(f)	Maintenance : (2% of direct capital)	<u>362 000</u>
	Total O & M costs	<u>5 578 000</u>

Annual fixed charge

Annual fixed charges depend on the interest rate and plant life :

For 10% interest and 20 year plant life the capital recovery factor = 0,1175 and for 15% interest and 15 year plant life the capital recovery factor = 0,1845.

$$\left[\text{capital recovery factor} = \frac{i}{1-(1+i)^{-n}} \right]$$

where i = interest rate
n = number of years]

Annual fixed charge = (Total capital costs - working capital)
x capital recovery factor.

2.31

At 10% and 20 years : $21\,749\,000 \times 0,1175$
 $= R2\,556\,000$

Total annual costs

Operation and maintenance	5 578 000
Annual fixed charge	<u>2 556 000</u>
10% and 20 years	<u>R8 134 000</u>

2.3.3 Unit production cost

Annual production from reverse osmosis plant
 $= 25\,000\text{ m}^3 \times 365 \times 0,9$ (plant factor)
 $= 8\,212\,000\text{ m}^3/\text{a}$ reclaimed water.

Annual production from brine concentrator
 $= 6\,250 \times 0,95 \times 0,9 \times 365$
 $= 1\,950\,000\text{ m}^3/\text{a}$.

Total annual production for plant with brine concentration
 $= 10\,162\,000\text{ m}^3/\text{a}$.

$$\text{Unit cost} = \frac{\text{Total annual cost}}{\text{Annual production}}$$

(a) For plant with brine concentration :

$$\begin{aligned} \text{Unit cost} &= \frac{\text{Total annual cost}}{\text{Annual production}} \\ &= \frac{8\,134\,000}{10\,162\,000} = R0,80/\text{m}^3 \end{aligned}$$

(b) For plant with sea disposal of brine, i.e. not taking brine concentration and disposal costs into account

Capital costs = 17 749 000

Annual fixed charges = 2 085 000
 Annual O & M costs = 3 628 000
R5 713 000

$$\text{Unit cost} = \frac{5\,735\,000}{8\,212\,000}$$

$$= R0,70/\text{m}^3$$

2.3.4 Sensitivity analysis

The major annual costs contributing to the final unit water cost are:

- (i) Annual fixed charge; which is a function of the total capital cost, the cost of money and the expected plant life.
- (ii) Membrane replacement cost; which is a function of membrane cost and membrane life.
- (iii) Energy cost; which is a function of the specific energy consumption ($\text{kW}\cdot\text{h}/\text{m}^3$) and the cost of electrical power.
- (iv) Brine disposal cost; which is a function of the degree of further treatment required and final route of disposal.
- (v) Pretreatment cost; which is a function of the required degree of pretreatment and which is very low in this case (about 5%).

The contribution of the most important cost items and the effect of changes in them on the final unit water cost are as follows :

2.3.4.1 Annual fixed charge

The contribution of the reverse osmosis capital cost (excluding membranes) to the annual fixed charge and unit water cost is :

$$\begin{aligned} & \text{R12 500 000} \times 0,1175 \\ & = \text{R1 470 000 annual charge.} \end{aligned}$$

which gives a contribution to the final unit water cost of $\text{R0},15/\text{m}^3$ of the total cost of $\text{R0},80$ or a 19% contribution.

The effect of variations in the reverse osmosis equipment cost on unit water cost is shown in Figure 2.6. Unit water cost is only moderately sensitive to changes in equipment cost, e.g. a 20% increase in equipment cost (from $\text{R}10 \times 10^6$ to $\text{R}12 \times 10^6$) results in an increase of only 4% (from $\text{R0},76/\text{m}^3$ to $\text{R0},79/\text{m}^3$) in unit water cost.

2.33

The economic feasibility of reverse osmosis is therefore not markedly affected by increases in reverse osmosis equipment cost.

2.3.4.2 Membrane replacement cost

The contribution of membrane replacement cost to the final unit water cost is R1 667 000 for 10 162 000 m³ per annum = R0,16/m³ or 21% of the total unit water cost.

If further brine treatment is excluded the contribution is R1 667 000 for 8 212 000 m³ per annum = R0,20/m³ or 29% of the unit water cost if the membrane life is taken as 3 years.

Figure 2.7 shows the effect of membrane life on the unit water cost. The exponential form of this curve shows a very steep increase in unit water cost if membrane life is shorter than two years while on the other hand the reduction in unit water cost when membrane life is longer than three years is relatively small.

The cost of membranes for a particular application and design production is determined mainly by the membrane area which is required to produce the design output at the end of the projected membrane life and by the actual membrane life. Membrane area, in turn is determined by the inherent membrane flux and the success with which this flux can be restored and maintained through pretreatment and cleaning.

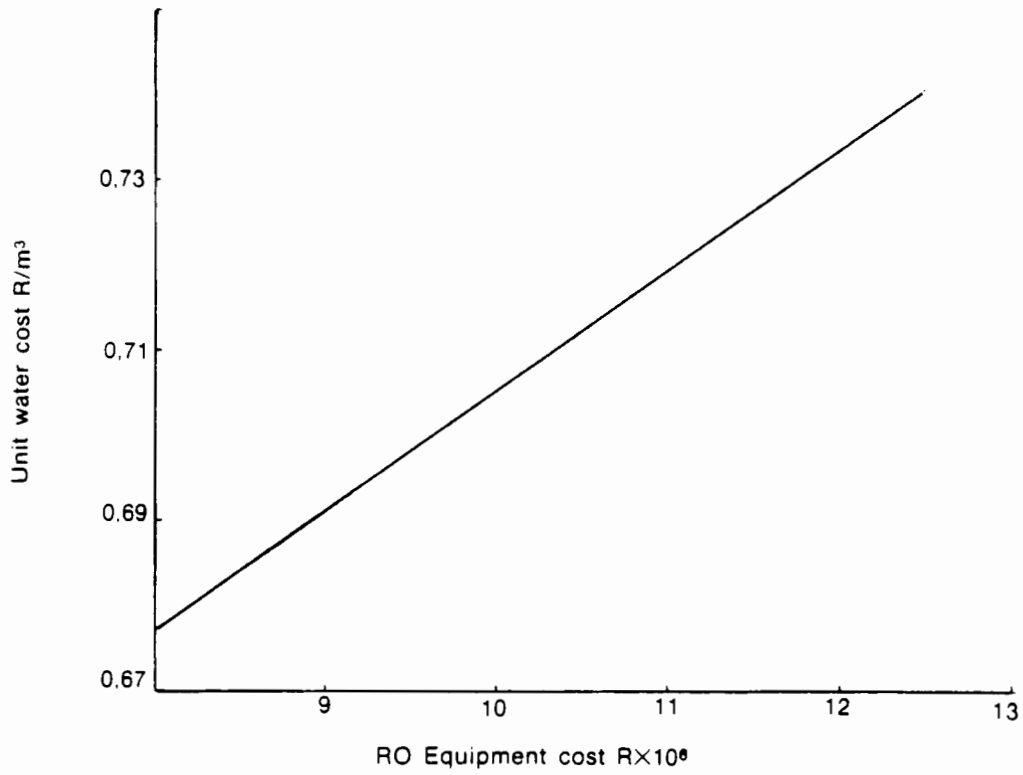


FIGURE 2.6: EFFECT OF VARIATIONS IN REVERSE OSMOSIS EQUIPMENT COST ON UNIT WATER COST

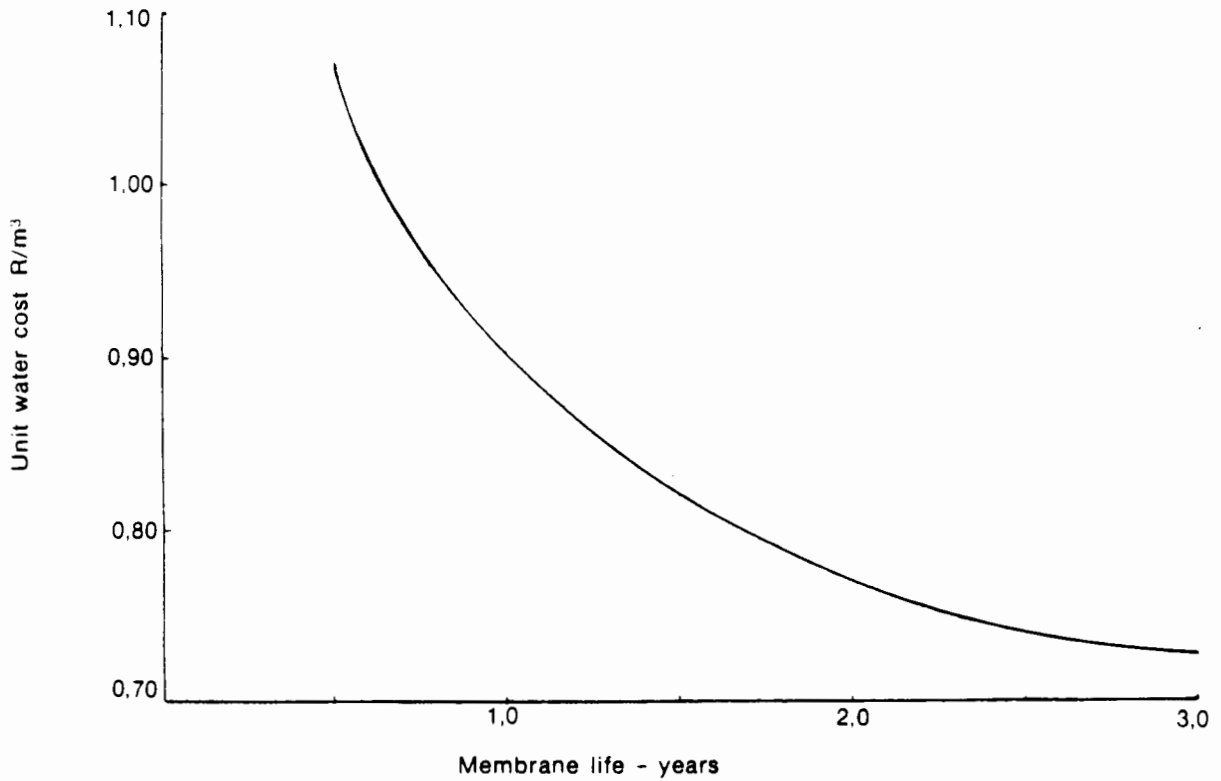


FIGURE 2.7: EFFECT OF VARIATIONS IN MEMBRANE LIFE ON UNIT WATER COST

It follows, therefore, that unit water costs will increase to unacceptable levels if membrane life is much shorter than 3 years, with the critical turning point in the curve at about 2 years. Membrane life can be defined as the period over which a module or set of membranes produces the designed volume of water at the designed rejection. It is, therefore, important to obtain practical information about these two aspects at least on pilot plant scale.

2.3.4.3 Energy cost

- (i) The contribution of energy costs to the final unit water cost (including brine treatment) is :

Reverse osmosis energy at 2,75 kW.h/m³ and R0,05/kW.h

= R1 129 000 for an annual production of 10 162 000 m³ per annum (reverse osmosis plus brine concentrator product water).

Reverse osmosis energy cost contribution to the unit water cost is R0,11/m³, or 14% of the unit water cost of R0,80/m³.

Brine concentrator energy at 20 kW.h/m³ and R0,05/kW.h.

= R1 950 000 giving a contribution of R0,19 to the unit water cost, or 24% of the unit water cost of R0,80/m³.

Total energy cost is therefore R0,30/m³ or 37,5% of the unit water cost.

- (ii) The contribution of energy costs if brine is disposed of without further treatment :

Reverse osmosis energy contribution to annual cost = R1 129 000 for a production of 8 212 000 m³.
 Energy contribution to unit water cost = R0,14/m³
 or 20% of the unit water cost of R0,70/m³.

Figure 2.8 shows the effect of electric power unit cost on unit water cost, while Figure 2.9 shows the effect of reverse osmosis specific energy consumption on unit water cost. These figures show that the economic viability of the process is significantly affected by the unit energy costs and to a lesser degree by the specific energy consumption.

The specific energy consumption of spiral wound modules in brackish water applications is about 1kW.h/m³ which would give a unit water cost of R0,73 compared to R0,80 for tubular systems with a specific energy consumption of 2,75 kW.h/m³.

2.3.4.4 Brine treatment costs

The major costs for brine disposal are fixed charges for capital redemption, and energy costs. Taking the annual fixed charge on the brine concentrator and energy costs and disregarding the contribution of brine treatment to other costs, the contribution of brine treatment to the unit water cost is :

Annual fixed charge on R4 000 000

= R 482 000

Energy cost = R1 950 000

R2 432 000 annual cost for a production of 10 162 000 m³ per annum, which gives a contribution of R0,24/m³ to the unit water cost of R0,80; i.e. a 30% contribution.

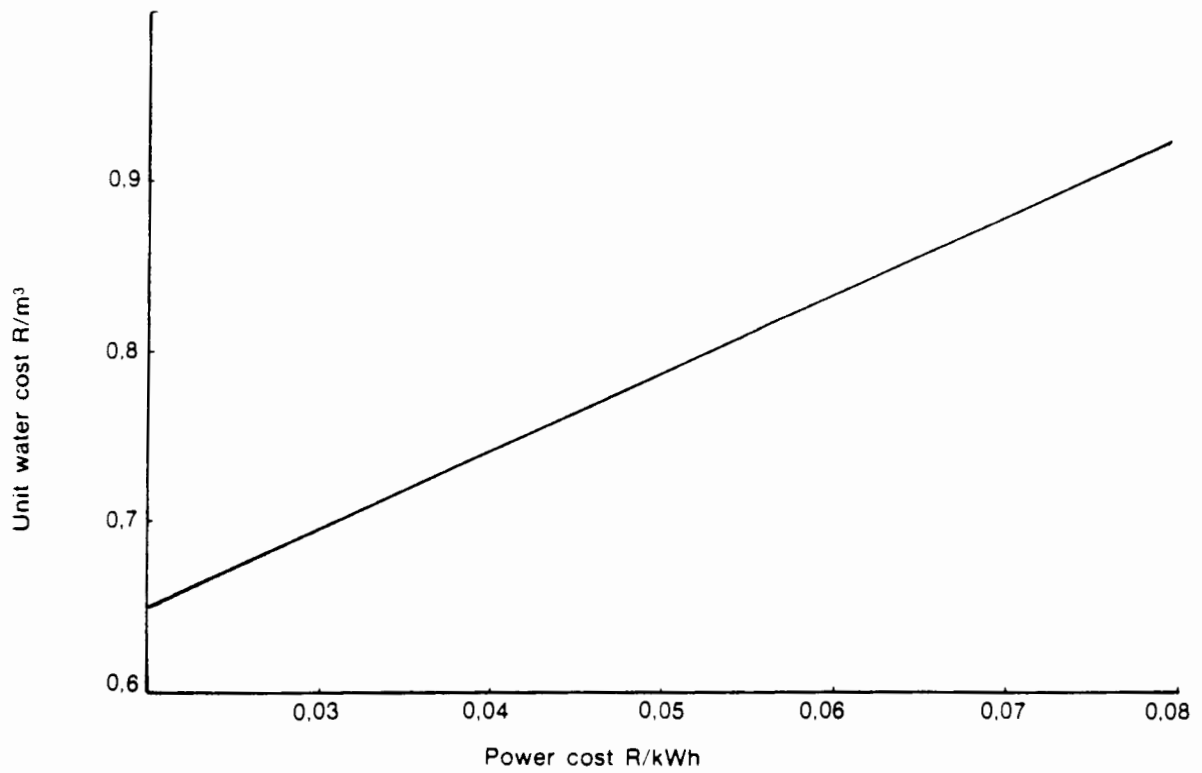


FIGURE 2.8: EFFECT OF VARIATIONS IN ELECTRIC POWER COST ON UNIT WATER COST

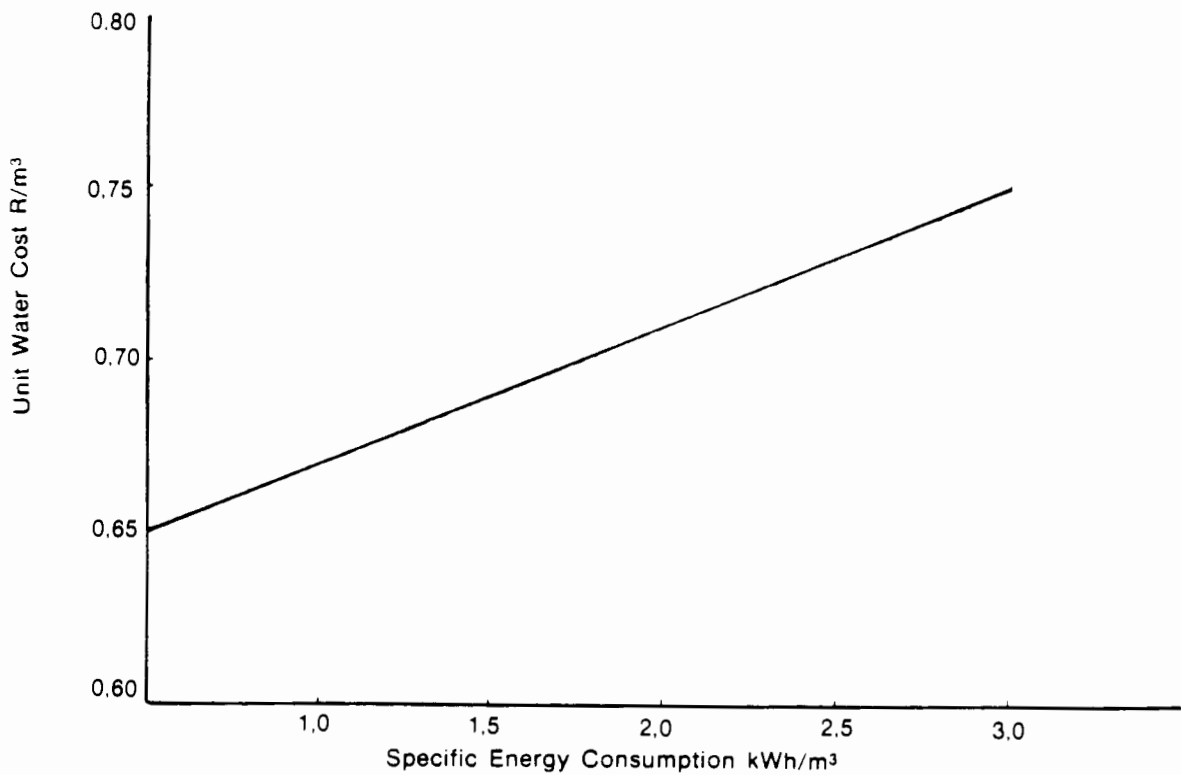


FIGURE 2.9: EFFECT OF VARIATIONS IN SPECIFIC ENERGY CONSUMPTION ON UNIT WATER COST

2.3.5 Economy of scale

Economy of scale is an important factor in desalination cost analyses, especially for distillation units. Reverse osmosis costs are less affected by plant capacity than are distillation costs as a result of the modular nature of reverse osmosis plants. Nevertheless, costs for small reverse osmosis units can be affected significantly by a number of cost factors, for example electric power development in remote areas, supervision, maintenance, etc.

Figure 2.10 shows the effect of plant capacity on unit water cost based on desalination of brackish water by reverse osmosis (Reed, 1982).

2.3.6 Conclusions

- (i) The estimated costs of reclaimed water at R0,80/m³ (including brine concentration and disposal) and R0,70/m³ (sea disposal of brine) are markedly higher than the cost of water from currently available conventional surface water supplies. However, the unit cost of water imported to a particular catchment will continue to increase as transfer distances get longer and terrain more difficult, especially for the transfer of relatively small volumes. The projected cost for water from the proposed Amatole Scheme to import water to the East London-King William's Town area is about R1/m³ while the marginal cost of transferring water from the Lesotho-Highlands scheme will be about R0,50/m³ (Triebel, 1985). It appears, therefore, that reclaimed water costs will not be so high as to exclude water reclamation as a water augmentation or water quality improvement option and that research in this field should continue.

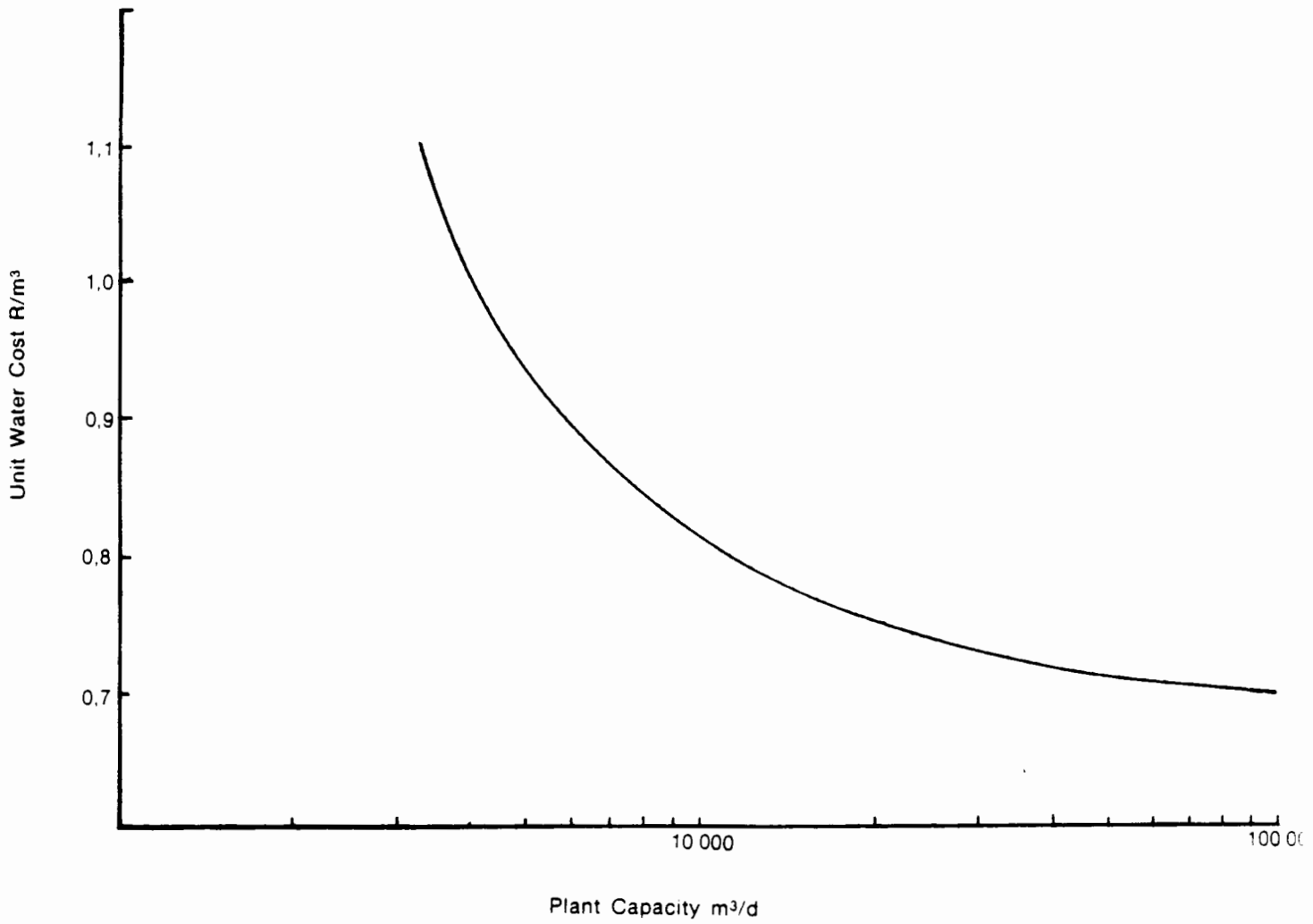


FIGURE 2.10 EFFECT OF VARIATIONS IN PLANT CAPACITY ON UNIT WATER COST

- (ii) Reverse osmosis will only be economically viable if a productive membrane life of about 3 years can be achieved and if membrane fluxes can be maintained at design rates. In order to obtain information on these aspects, a pilot plant study was conducted with the objective to determine pretreatment requirements and to assess membrane cleaning procedures needed to maintain membrane fluxes at acceptable levels. This information was required before a decision on further research and a larger-scale demonstration plant could be taken. These pilot plant studies are described and discussed in Chapter 3.

2.4 DESK STUDY ON THE REJECTION OF CONTAMINANTS BY REVERSE OSMOSIS

2.4.1 Introduction

The concept of direct reuse of reclaimed water in domestic supplies is opposed by many health authorities for the reason that information about the identity and nature of mainly organic constituents in sewage is lacking and that surveillance testing for the presence of such compounds in reclaimed water is therefore not possible. It is, therefore, also not possible for health authorities to guarantee the absolute safety of reclaimed water, especially with respect to the possible long-term effects of potential carcinogens which may be present in reclaimed water. Some suspected carcinogens have been identified in drinking water where indirect reuse occurs. Fielding *et al.* (1981) identified 324 organic compounds in treated drinking water in England, some of which are suspected carcinogens.

In view of these uncertainties it is essential that all organic compounds which are potentially harmful in any way should be removed to acceptable levels. Furthermore, since the bulk of organic material in sewage and in drinking water cannot be characterized (Kraybill 1981), it would be prudent to reduce all organic material to the lowest levels possible.

2.41

This desk study was, therefore, conducted to determine the efficiency of reverse osmosis to remove organic material in general and certain specific organic compounds from water.

2.4.2 Rejection of collective groups of dissolved organic matter by reverse osmosis membranes

The concentration of dissolved organic matter in water is most conveniently determined by collective parameters such as total organic carbon (TOC) or chemical oxygen demand (COD). Other collective parameters give information on the concentration of specific groups of organics, for example : total organohalogens (TOX), or even more specific : purgeable organohalogens (POX) and non-purgeable organohalogens (NPOX).

These and other collective parameters are useful in monitoring the performance of water reclamation processes since some of them can be determined continuously and in a short time. They, furthermore, give information on removal of a broad spectrum of organics and can therefore be used as surrogate parameters for other organic compounds. Rejection of specific organic compounds is considered in Section 2.4.3.

(i) Rejection of COD and TOC

Organic material in waste water as expressed by COD and TOC is rejected very effectively by reverse osmosis membranes. Figures reported in numerous studies range from lows of 65% for COD rejection by cellulose acetate (Cruver and Nusbaum 1974) to 99% rejection of TOC from lime clarified secondary effluent (Argo, 1984).

It is evident from reports by Chian et al. (1977), Welcher (1977), McCarty et al. (1980, 1982), Argo (1979, 1980), Argo et al. (1984) and Jekel and Roberts (1980) that removal of COD and TOC is a function of (a) the type of membrane material (b) the "tightness" of the membrane as reflected by its rejection of NaCl and (c) the degree of treatment of the sewage.

The composite aromatic polyamide membranes (Chapter 3.2) which have a very high NaCl rejection also reject organic material measured as COD and TOC very effectively. Rejection figures ranging from 88% to 99% have been reported for chemically clarified activated sludge effluent. Cellulose acetate membranes also reject organics very effectively but not as well as the polyamide membranes. Figures 2.10 and 2.11 reproduced from Argo (1980) show the removal of COD and TOC by a full-scale plant, Water Factory 21, employing cellulose acetate membranes. For 95% of the time the reverse osmosis permeate had a concentration of less than 4 mg/ℓ COD and less than 1,7 mg/ℓ TOC from feedwater with 30 mg/ℓ COD and 13 mg/ℓ TOC.

It should be pointed out that organic matter measured as COD and TOC respectively is not removed to the same degree under all circumstances. The reason is that COD measures the chemically oxidizable material while TOC measures the actual carbon content. The ratio COD/TOC decreases therefore as concentrations become lower. Rickett and Hunter (1977) found that the COD/TOC ratio decreases from 3,8 for settled sewage to 2,6 for secondary effluent, while a ratio of about 1,2 is typical for reverse osmosis effluents.

(ii) Rejection of organics determined as ultraviolet absorbance (UVA)

Ultraviolet absorbance at 275 nm and at 254 nm is a measure of the aromatic dissolved organics present which will absorb ultraviolet radiation at the specific wavelength. Ultraviolet absorbance (UVA) is very easy to measure, it can be done very accurately and continuously and is highly reproducible. It is, however, not certain to what extent changes in the UVA will reflect the efficiency of treatment processes such as reverse osmosis and activated carbon adsorption with respect to removal of organic material of interest.

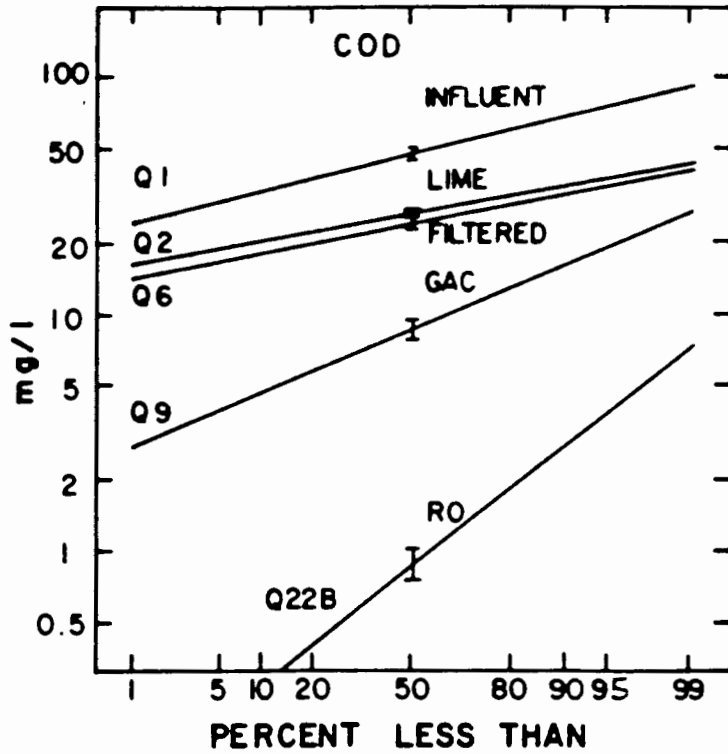


FIGURE 2.10: REMOVAL OF COD BY DIFFERENT PROCESSES AT WATER FACTORY 21 (ARGO, 1980)

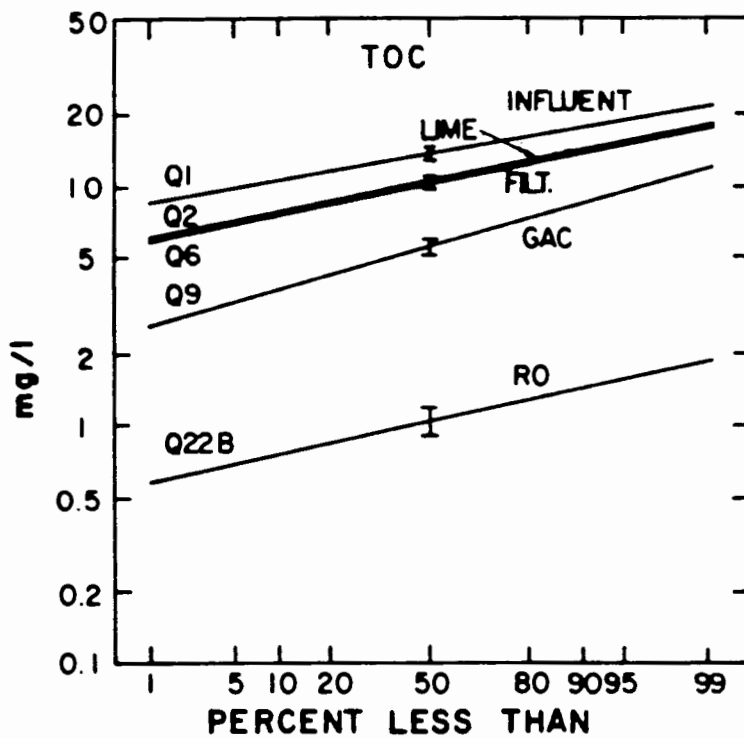


FIGURE 2.11: REMOVAL OF TOC BY DIFFERENT PROCESSES AT WATER FACTORY 21 (ARGO, 1980)

McCarty et al. (1982) report lower removals of organics when measured by UVA than of TOC and COD by reverse osmosis at Water Factory 21, but higher removals of organics when measured by UVA than TOC and COD by activated carbon. The mean overall removal of organics when measured by UVA by the whole plant was 88% compared to 97% removal of COD.

Vail and Barnard (1986) report mean rejections of 95% by UVA at both 254 and 275 nm from a chlorinated secondary effluent by cellulose acetate membranes, compared to 89% removal of COD.

De Villiers et al. (1984) found typical TOC reductions of 88% from extensively treated secondary sewage effluents compared to 75% reduction of organics when measured by UVA.

These differences may be a result of the different characteristics of the effluents treated in each case. In addition UVA increases upon chlorination up to the breakpoint whereafter it decreases. So the chlorination procedures also play an important role in overall plant performance as reflected by UVA. These points emphasize the caution required when using UVA to monitor process or plant performance.

It appears, therefore, that UVA is not a suitable substitute for TOC as it does not change in the same manner as TOC in different unit processes. For example, the ratio of UVA/TOC for sand filter effluent is about 16 000, and increases to 22 000 after chlorination and is reduced to 18 000 by reverse osmosis.

However, UVA may be suitable to monitor the organic removal efficiency of a particular process if the UVA/TOC or UVA/COD relationships are determined over a period of time and if variations that may occur have been established. The big advantage of UVA is that it can be monitored continuously at a relatively low cost and can therefore be used to monitor changes in the chemical composition of the influent to the plant or any malfunctioning of a process.

(iii) Rejection of chlorinated organic compounds and precursors

Halogenated organic compounds are important in evaluating the quality of drinking water since the presence of these compounds may indicate pollution by industrial discharges. Furthermore, halogenated compounds are generally toxic in nature as is reflected by the fact that more than half of the priority pollutants identified by the US Environmental Protection Agency (1977) are halogenated organics.

Collective parameters for halogenated compounds include total halogenated organics (TOX) and the purgeable volatile fraction (POX) and non-purgeable (NPOX) fraction as one group. The second group includes trihalomethanes, and its different fractions, trihalomethane formation potential THMP, the instantaneous value THM and the terminal value THMT. A third group constitutes the halogenated pesticides.

Only limited data are available on the removal of the first group by different processes. Jekel and Roberts (1980) give data on TOX, POX, NPOX and TOC for effluents from different treatment processes at Water Factory 21. A summary of their data is given in Table 2.4

TABLE 2.4 CHLORINATED ORGANICS IN WATER FROM WATER FACTORY 21 (JEKEL AND ROBERTS, 1980)

<u>Treatment process</u>	<u>TOC</u> mg/l	<u>TOX</u> μmol/l	<u>POX</u> μmol/l	<u>NPOX</u> μmol/l
lime treatment	10,0	3,46	0,39	3,07
NH ₃ stripping	-	3,02	0,06	2,96
chlorination	-	6,27	0,30	5,97
activated carbon	6,2	4,01	0,18	3,83
chlorination		4,71	0,34	4,37
reverse osmosis	2,6	0,94	0,07	0,87

It should be pointed out that included under the reverse osmosis process is an air stripping tower for decarbonation and it appears that the reduction of 80% in POX by reverse osmosis is attributable to air stripping of the volatiles rather than removal by the cellulose acetate membranes.

This table shows that reverse osmosis is much more effective for the removal of the non-volatile fraction NPOX than activated carbon, both in terms of removal efficiency as well as the concentration that can be achieved.

The second group of halogenated organics, the trihalomethanes, is included in the NPOX fraction discussed above and is also poorly removed by reverse osmosis membranes but effectively removed by air stripping. The trihalomethane formation potential (THMP) is an indication of the amount of precursor material present and is determined as the amount of THM formed when excess chlorine is added to a water sample and the chlorination reaction allowed to proceed to completion. This method is not very accurate and not very reproducible especially when very large chlorine dosages are required to oxidize ammonia so that free chlorine is formed. McCarty et al. (1982) reported removals of THMP by reverse osmosis to vary from 19% to 88%. The variability in these results is such that it is not possible to determine statistically significant removal values.

The removal of pesticides by reverse osmosis membranes was studied by Chian et al. (1975). Chlorinated pesticides including aldrin, lindane, dieldrin, heptachlor and DDT as well as organophosphorus pesticides were removed to very low levels at rejections of 98% or better. The more polar compounds especially randox and atrazine (herbicides) which have a higher water solubility showed lower rejections by the cellulose acetate membranes; 72% and 84% respectively.

In natural waters pesticides are normally complexed with humic material and these complex compounds are very effectively rejected by reverse osmosis membranes because of their high molecular mass. It can therefore be expected that the removal of pesticides from water containing humic and fulvic material will be higher than reported for solutions in pure water.

In summary, non-volatile chlorinated organic compounds are rejected very effectively by reverse osmosis membranes while the volatile fraction largely permeates membranes. Provision will therefore have to be made in a water reclamation plant for alternative processes to remove volatile organics such as chloroform which is a suspected carcinogen.

2.4.3 Rejection of specific organic compounds

The removal efficiency of organic compounds by reverse osmosis membranes depends on the type of membrane used and on the properties of the specific compound or group of compounds under consideration. For example, phenol is removed very effectively (99%) by the composite PEC-1000 membrane (Kurihara *et al.*, 1981); it is removed effectively by the composite FT-30 membrane (94%) but is virtually not removed by cellulose acetate membranes, which may even show negative rejections (Matsuura and Sourirajan 1971).

In water reclamation applications removal of organics with health implications is of primary concern. Several studies on the removal of pesticides, USEPA priority pollutants, trihalomethanes and individual compounds by different membranes are reported.

Fang and Chian (1976) studied the rejection of 13 polar low molecular mass organic compounds by 12 reverse osmosis membranes. It can be concluded from these studies that membranes made of cellulose acetate and its derivatives (cellulose triacetate and cellulose acetate butyrate) yield very low degrees of separation for the polar organic compounds in spite of very good NaCl rejection (97 to 99,5%). Membranes made of aromatic polyamide and cross-linked

polyethylenimine with a 98 to 99,5% rejection of NaCl showed a much higher rejection on average of the group of organics. They expressed the overall separation of solutes as the anticipated separation of a mixture having a concentration of 1 000 mg/ℓ TOC contributed on an equal weight basis by each of the thirteen test compounds : methanol, ethanol, i-propanol, acetic acid, formaldehyde, acetone, ethyl ether, urea, glycerol, phenol, hydroquinone, aniline, methyl acetate. The overall rejections given as 12,82% for cellulose acetate, 69,83% for polyethylenimine and 63,48% for aromatic polyamide therefore do not have any significance because the group of organics includes compounds, such as i-propanol and glycerol which are well rejected by all membranes and others such as methanol which are poorly rejected by all . The rejections given for individual compounds and membranes are more meaningful.

Light (1980) reported on bench scale reverse osmosis tests on the removal of chemical carcinogens from water and waste water by two different aromatic polyamide membranes. Fourteen individual water soluble chemicals which are representative of eight groups of organic chemical carcinogens were investigated. Included in the list are three widely used solvents and a detergent. The results from this study confirm results from other studies viz. that removal efficiencies are high for high molecular mass organics such as malathion and methyl orange, and low for small polar chemicals such as formaldehyde and ethanol.

The most comprehensive study on the removal of trace organic chemicals by advanced treatment processes including reverse osmosis was done by McCarty et al. (1980, 1982) at Water Factory 21. They identified 25 organic priority pollutants in the influent to the plant and monitored their removal by the different processes. These compounds were present in very low concentrations in the influent to the plant with the highest concentrations chloroform at 3,5 g/ℓ and bis (2-ethylhexyl) phthalate at 11 g/ℓ. Since influent concentrations were very low and because chlorinated compounds were formed as

well as removed in the plant, removal efficiencies varied considerably, so that no firm conclusion can be reached on removal efficiencies. The concentrations of these compounds in the final water were far below 1 $\mu\text{g}/\ell$ with the exception of chloroform (1,8 $\mu\text{g}/\ell$) and bis (2-ethylhexyl) phthalate (1,2 $\mu\text{g}/\ell$).

In spite of these differences between membranes certain general conclusions on rejection may be made :

- (i) Mainly low molecular mass (<150 molecular mass units) relatively volatile organic compounds permeate reverse osmosis membranes.
- (ii) The tighter the membrane (i.e. the higher the rejection of TDS) the better the rejection of organic compounds.
- (iii) The structure of the organic molecule under consideration is important in determining rejection. Small, linear molecules permeate membranes better than do bulky branched molecules with the same molecular mass (Duvel and Helfgott 1975).
- (iv) The physico-chemical properties of the solute play a major role in certain cases, e.g. in the case of cellulose acetate and phenol. It has been shown that the permeation of cellulose acetate membranes by organic compounds can be correlated with the ability to form hydrogen bonds (Garry-Bobo et al., 1969).

2.4.4 Removal of inorganic compounds

Reverse osmosis membranes are very effective in removing most inorganic compounds (McCarty et al., 1982). Exceptions of interest are nitrates and other oxidized nitrogenous compounds which are not effectively removed by cellulose acetate membranes. They are, however, removed very effectively by aromatic polyamide and other non-cellulosic membranes.

2.5 CONCLUSIONS

The following overall conclusions can be drawn from the desk studies :

2.5.1 Potential role of reverse osmosis

A clear and definite potential role for reverse osmosis exists in many different applications in South Africa.

- (i) A number of potential applications for brackish water desalination exists at present in the more arid parts of the country. No further research is required for this type of application.
- (ii) The major potential short to medium term (10 years) applications can be expected in the treatment and reclamation of industrial effluents with relatively high concentrations of total dissolved solids. These include mining waters, cooling tower blowdown and effluents from different industries. Further research is required for some of these applications.
- (iii) In the medium to long term a very important role is projected for reverse osmosis in water reclamation applications, both for direct and indirect reuse situations. Further research is required as discussed below.

2.5.2 The economic viability of reverse osmosis as a water reclamation process

- (i) The estimated reclaimed water unit cost of R0,80/m³ is relatively high when compared to the water cost from existing sources. However, it compares favourably with the cost of water from some interbasin transfer schemes. On economic grounds, water reclamation by reverse osmosis, therefore, appears to be a viable process to augment water supplies or to improve the quality of existing supplies.

- (ii) The sensitivity analysis shows that the unit water cost is very sensitive to membrane life. The critical break in the cost curve is at about 2 years where costs start to increase very sharply.
- (iii) Further studies on pilot plant scale are required to get information on the maintenance of membrane flux levels and membrane rejection in order to determine projected membrane life and to decide on the viability of large-scale applications.

2.5.3 Membrane rejection characteristics

- (i) Reverse osmosis membranes reject dissolved organic material in water effectively. Composite aromatic polyamide membranes, in particular, have a very high rejection (90% and up to 99% of COD and TOC).
- (ii) The organic compounds that do permeate the membranes are mainly volatile low molecular mass organics. Some of these compounds have been identified as suspected carcinogens so that it is important to determine and quantify the factors that affect removal of low molecular mass organics by different membranes.

2.6 RECOMMENDATIONS

The main recommendations are :

- (i) That pilot plant studies be undertaken in order to evaluate procedures to maintain membrane flux levels at design values so as to be able to project membrane life and membrane performance in full-scale applications. These are the main factors that will affect the economic viability of reverse osmosis in full-scale water reclamation applications. These studies are discussed in Chapter 3.

- (ii) That a fundamental study be conducted on the rejection of low molecular mass organics by reverse osmosis membranes. Furthermore, that an attempt is made to develop a simple predictive model for the rejection of organic compounds of interest. These laboratory studies are described and discussed in Chapter 4.

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CHAPTER 3

PILOT PLANT STUDIES

3.1 INTRODUCTION

It was concluded from the desk studies that pilot-scale information is necessary to determine membrane flux levels that can be maintained under practical operating conditions. The rate of decline in membrane flux levels and in rejection characteristics determines productive membrane life which significantly affects the reclaimed water cost and therefore the economic viability of reverse osmosis in water reclamation applications.

The objectives of the pilot plant studies were :

- (i) to determine the effects of feed water pretreatment and membrane cleaning on flux levels and rejection over a relatively long period;
- (ii) to monitor membrane performance with respect to the removal of dissolved organic substances.

The pilot plant research was carried out by the National Institute for Water Research (NIWR) of the Council for Scientific and Industrial Research (CSIR) under contract to the Water Research Commission (WRC). The author initiated this project, defined the objectives and drew up the research programmes. The author was responsible for the overall design and control of the project but the day to day running and control was conducted by the NIWR. The pilot plant was situated in the Bellville regional laboratory of the NIWR. The Tables and Figures on the pilot plant work in this Chapter are reproduced from the contract report submitted by the CSIR to the WRC (De Villiers et al., 1984).

3.2 PILOT PLANT PROCESS DESIGN

The process design of the pilot plant was based on the following assumptions and requirements :

3.2

- (i) The pilot plant configuration and layout should be similar to that of a module of a full-scale plant and the design performance should resemble that of a full-scale plant.
- (ii) Well oxidized activated sludge effluent should be used as feed and should be pretreated to a good quality with respect to its fouling potential in order to minimize fouling of the membranes.
- (iii) Water recovery should be maximized but should be limited initially to prevent excessive fouling of the membranes in the initial stages.
- (iv) A single module of an alternative membrane system should be evaluated in parallel to the pilot plant as a control to the performance of the membranes in the pilot plant.
- (v) A control experiment should be conducted with limited pretreatment to determine the role of pretreatment in the control of fouling. This requirement was subsequently dropped because the municipality of Port Elizabeth and Bintech (Pty) Ltd decided to conduct a similar study using the same membranes as selected for this study but using only limited pretreatment, in effect therefore serving as a control study. (See discussion in Section 3.5).

3.2.1 Membrane selection

Different reverse osmosis membrane materials and membrane systems are available for water reclamation applications. The membrane materials include cellulose acetate and its derivatives and aromatic polyamide as well as a number of newer polymers, while the systems include spiral wound, tubular, hollow fibre and plate and frame systems.

Cellulose acetate membranes : The first successful membranes were prepared from cellulose acetate and mixtures of cellulose acetate and its derivatives (Reid and Breton, 1959; Loeb and Sourirajan, 1962).

3.3

These membranes have been used successfully in many applications over long periods. The main disadvantage of cellulose acetate membranes is that they are susceptible to hydrolysis at pH's outside the optimum range of about 4 to 6 resulting in deterioration of performance. Hydrolysis is accelerated by high temperatures 35°C and free chlorine in the feed water 1,0 mg/ℓ. These membranes are also prone to microbiological attack since bacteria can attach to the membrane surface and utilize the cellulose acetate as a feed source.

Aromatic polyamide membranes were developed towards the end of the 1960's by Richter and Hoehn (1971) and Orofino *et al.* (1970). These membranes are superior to cellulose acetate membranes in some respects i.e. they are not susceptible to hydrolysis and biological attack, they have very high perm-selectivity and they have a much higher rejection of non-ionized low molecular mass organic solutes than cellulose acetate. Aromatic polyamide membranes can tolerate pH's in the range of 2 to 12 for cleaning purposes and can operate in the range of 4 to 10 and can operate at temperatures of up to 65°C compared to cellulose acetate membranes with a pH range of 4 to 6 and temperatures up to 35°C.

The major disadvantage of aromatic polyamide as membrane material is that it is susceptible to oxidation by free chlorine in solution. Free chlorine levels should therefore not exceed 0,1 mg/ℓ. Another disadvantage of aromatic polyamide membranes is that they have lower water permeabilities than cellulose acetate membranes. However, this disadvantage can be overcome by providing a high membrane area to volume ratio such as in the hollow fibre configuration or by making the membrane extremely thin and incorporating groups such as carboxylic or sulphonic groups in the polymer structure to make it more hydrophilic.

Composite membranes are not manufactured according to the gel polymerization technique used for cellulose acetate and aromatic polyamide membranes but rather by interfacial polymerization of monomers at the surface of a microporous substructure (Cadotte and Peterson, 1981). A composite membrane consists of a porous substructure such as an ultrafiltration membrane and a very dense salt rejecting skin on the substructure.

3.4

An example of a composite membrane is the FT-30 membrane manufactured by Filmtec Corporation which consists of an aromatic polyamide skin on a polysulphone ultrafiltration membrane (Larson et al., 1982). Polysulphone membranes have excellent chemical and temperature resistance, are chemically unreactive and are therefore ideally suited as support membranes.

The polyamide skin is made by interfacial polymerization of an aromatic amide on the polysulphone followed by cross linking of the polymer.

Another example of a composite membrane is the PEC 1000 membrane manufactured by Toray Ind. of Japan (Kurihara et al., 1981) where the active layer is manufactured from cross-linked polyether on a polysulphone support membrane. This membrane has a very high rejection for NaCl (>99,5%). It also shows very good rejection of the lower molecular mass dissolved organic solutes e.g. in the order of 90% for ethanol compared to about 75% rejection of ethanol by the FT 30 membrane. Both these membranes have much higher rejections of the low molecular mass organics than cellulose acetate membranes.

In summary, both cellulose acetate and composite membranes are suitable for water reclamation applications. The main advantage of cellulose acetate membranes is that they can tolerate free chlorine in solution at low concentrations which is important in water reclamation to control micro-organisms. On the other hand composite membranes have excellent rejection characteristics and therefore produce a better quality final product, but they are very sensitive to free chlorine in solution.

In view of these advantages of cellulose acetate and the fact that tubular cellulose acetate membranes are manufactured locally in South Africa at very competitive prices it was decided to use these membranes in the pilot plant. It was further decided to evaluate one module of a tubular composite aromatic polyamide membrane in parallel to the pilot plant.

3.2.2 Selection of membrane configuration

The selection of tubular cellulose acetate membranes for the pilot plant is not in line with the general trend of the almost exclusive use of spiral wound or hollow fibre modules in reverse osmosis plants in general. There are, however, certain advantages in using tubular membranes in water reclamation applications, the most important of which is the accessibility to clean the membranes using sponge balls or high speed flushing. The main disadvantages of tubular membranes are their relatively high cost compared to spiral wound and hollow fibre membranes, and the relatively high specific power consumption of about 2,8 kW.h/m³ compared to less than 1 kW.h/m³ for the other types. However, the competitive prices of the locally manufactured tubular membranes and the fact that unit water cost is not very sensitive to specific energy consumption (Section 2.3) reduced the importance of these disadvantages. In view of its major advantage with respect to control of fouling, the tubular system was selected for the pilot plant.

The relative merits of different membrane configurations are summarized below.

<u>Tubular</u>	<u>Spiral</u>	<u>Hollow fine fibre</u>
1. Large flow passages, high velocities and turbulent flow can be achieved. Not very susceptible to fouling. Requires limited pretreatment.	Long restricted flow path, susceptible to fouling, requires fair degree of pretreatment.	Very restricted passageways. Highly susceptible to fouling, requires extensive pretreatment.
2. Can be cleaned mechanically with relative ease e.g. by sponge balls.	Mechanical cleaning not possible. Rinsing and flushing with detergents and chemicals are fairly effective.	Cannot be cleaned mechanically. Not readily flushed.
3. Low membrane density 100 to 300 m ² /m ³ .	Intermediate density 300 to 1 000 m ² /m ³ .	Very high density 10 000 to 30 000 m ² /m ³ .

3.6

<u>Tubular</u>	<u>Spiral</u>	<u>Hollow fine fibre</u>
4. Relatively high membrane costs per installed m ³ product water.	Intermediate cost per installed m ³ product.	Relatively low cost per installed m ³ .
5. Pretreatment : Relatively simple pretreatment required. Low cost.	Intermediate pre-treatment required. Relatively high cost.	Extensive pretreatment required. High cost.
6. Individual damaged membranes may be replaced in some configurations.	Whole element must be replaced.	Whole permeator must be replaced.

3.2.3 Design of plant configuration

The layout of membranes or the reverse osmosis plant configuration determines to a large extent flow conditions inside the membranes and therefore also membrane performance and overall plant performance. One of the important parameters in the design of the plant configuration is the design product water recovery which is product flow divided by feed flow expressed as a percentage. The higher the recovery, the more water and the less brine is produced and the more economical is the whole process. However, due to the effects of concentration polarization and restrictions on brine concentration and on flow rates, the water recovery in a single set of modules is usually limited. In order to achieve higher water recoveries, multi-staging of reject streams may be employed where the reject from the first set of modules is used as feed to a second set and the reject from this stage used as feed for a third set. In this way water recoveries of 75 to 90% can be achieved for brackish waters. Alternatively a larger number of modules may be used in series to increase the water recovery, provided that due care is taken to maintain flow velocities above predetermined minimum values in the final modules.

3.7

In flowing across a membrane the feed becomes more and more concentrated as relatively pure water passes through the membranes. This is most pronounced at the membrane surface where the salt concentration can be much higher than in the bulk of the feed stream. The phenomenon is known as concentration polarization and has a number of negative effects on membrane performance, viz. precipitation of salts such as calcium sulphate may occur as a result of the high concentration at the membrane surface; a reduced flux may result caused by the total increase in osmotic pressure and thus a reduction in effective driving force; salt passage through the membrane may increase as a result of a higher salt concentration at the membrane surface.

In passing from one stage to the following in the reject staging configuration the feed gets more and more concentrated accentuating the effects of concentration polarization in the latter stages. Turbulent feed flow at the membrane surface counteracts concentration polarization and it is therefore important to maintain adequate flow velocities. For this reason reject multi-staging is normally done in a tapered configuration of say 4, 2, 1 modules in the 1st, 2nd and 3rd stages respectively.

In order to achieve a water recovery of 80% the plant was designed in a tapered configuration as shown in Figure 3.1. Thirty modules were used in the plant, each module having an effective membrane area of 1,75 m². The modules each contain 19 membrane tubes, 12,7 mm diameter, linked in series, supported in a stack of perforated polymer discs housed in a 2 500 x 102 mm aluminium tube. The membrane tubes are interconnected by moulded polymer 180° connectors, the module end assembly being encapsulated in an epoxy resin.

The tapered flow array was designed in such a manner than the linear velocities in all the modules remained above 0,7 m/s.

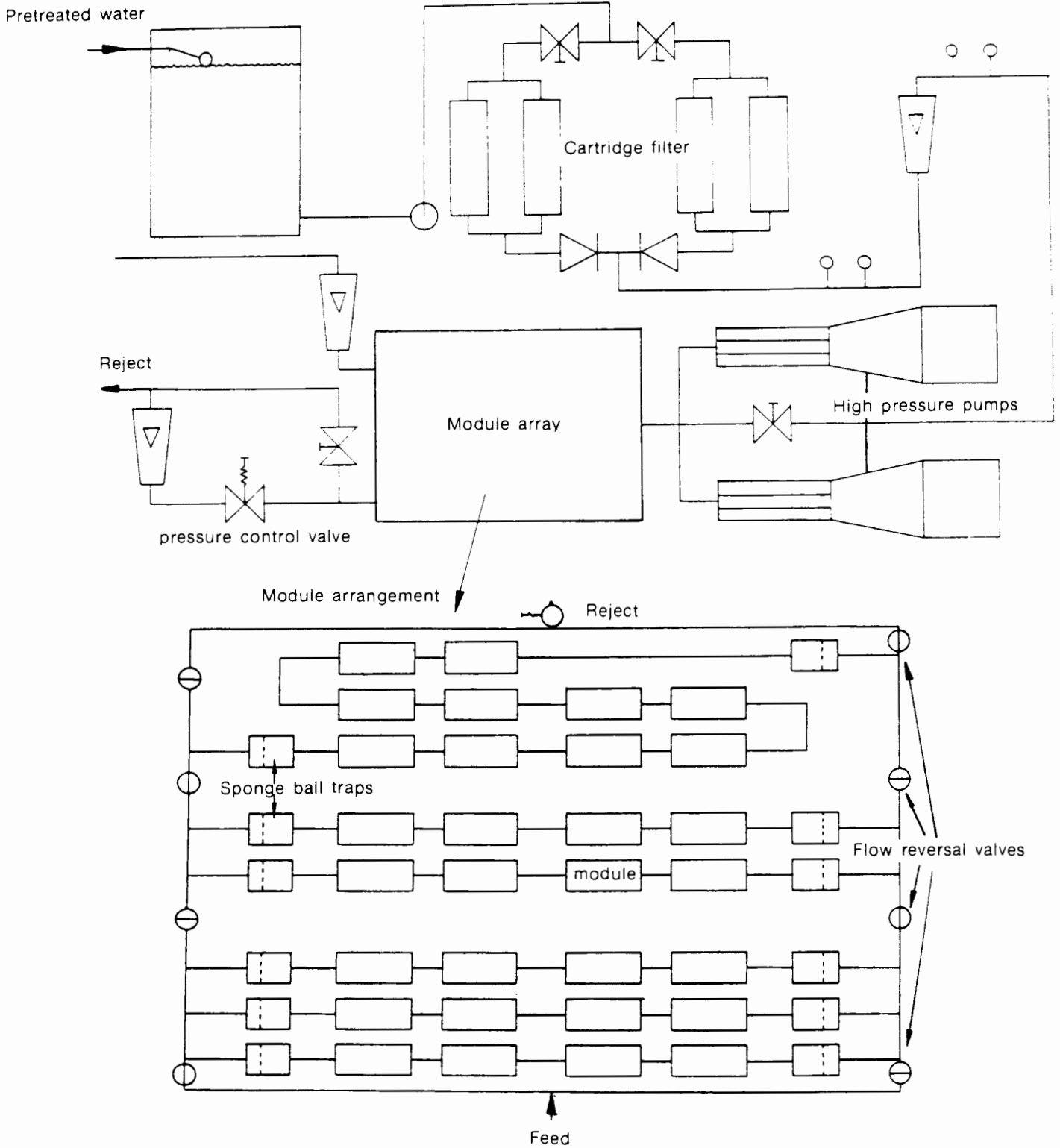


FIGURE 3.1: FLOW DIAGRAMME OF PILOT PLANT

The design membrane performance (manufacturer's specification) at 4 000 kPa pressure and at 20°C operating on a 2 000 mg/ℓ NaCl solution is given as a salt rejection of 90% and a flux of 571 ℓ/m².d.

Also incorporated in the plant was a flow reversal system and an automatic sponge ball system as is shown in Figure 3.1. A sponge ball trap was fitted to each end of the series module trains. When flow reversal occurs, two sponge balls are passed through each train and are caught in the sponge ball trap at the other end. The flow reversal valves are linked together and are actuated by a double acting pneumatic cylinder controlled by an electronic timer.

3.2.4 Selection of pretreatment system

As is mentioned in Section 3.1 it was decided to pretreat the feed water to a relatively good quality so as to prevent excessive membrane fouling.

3.2.4.1 Feedwater characterization

Conventional parameters such as turbidity or chemical analyses of the feedwater provide some qualitative insight into the fouling potential of a feedwater with regard to particulate fouling or the likelihood of precipitation of sparingly soluble salts etc., but it has been shown that they are of no real value as an indication of the fouling tendency in water reclamation applications (Winfield, 1979; Comstock, 1980).

Fouling tests which have been developed specifically for reverse osmosis applications are all based on the rate of filtration through a 0,45 micron filter disc at a constant pressure (210 kPa) (Patel et al., 1976).

3.10

These tests give a plugging or fouling index or factor which may be expressed as a percentage :

$$\%PI = 100 \left(1 - \frac{t_i V_f}{t_f V_i} \right)$$

where t_i = time for initial sample
 t_f = time for final sample
 V_i = volume of initial sample
 V_f = volume of final sample.

For the constant volume tests $V_i = V_f$ and for the constant time tests $t_i = t_f$.

A further variant of this test gives a Silt Density Index (SDI) which is computed by dividing the Plugging Percentage by the overall time of the test, usually 5 or 10 or 15 minutes.

These filtration tests give a relatively good indication of the general quality of feedwater with respect to the presence of colloidal or other plugging material retained by a 0,45 micron filter. However, in practice especially for polluted feedwater there is no fixed correlation between any of these indices and the actual rate or extent of fouling of reverse osmosis membranes. In spite of this, the Plugging or Fouling Index and the Silt Density Index are the most widely used fouling tests and many reverse osmosis plant manufacturers specify limits for these indices for their membranes. Du Pont, for example, specifies a maximum Plugging Index of 45% (210 kPa and 15 minutes), which is equivalent to an SDI of 3,0 for their hollow fine fibre permeators.

3.11

Schippers and Verdouw (1980) improved on the above tests by developing a Modified Fouling Index (MFI) based on classical filtration theory, where :

$$\text{MFI} = \frac{\eta_{20}}{\eta} \frac{\Delta P}{210} \tan \alpha$$

η_{20} = viscosity at 20°C

η = viscosity at temperature of test

ΔP = applied pressure (kPa)

$\tan \alpha$ = slope of the straight line portion of a plot of the reciprocal of the volumetric flow rate (t/V total) against the accumulated filtrate volume (V total).

The basic difference between the MFI and the other indices described above lies in the interpretation of the results. Schippers et al. (1980) found a better correlation between MFI of polluted waters with actual membrane fouling than with the other indices. However, the MFI test is based on the same test conditions as the other tests which poorly simulate actual reverse osmosis operating conditions. In an actual reverse osmosis module the feed flows tangentially along the membrane surface at relatively high velocities. In the fouling tests the feed flow is perpendicular to the membrane. Further, the 0,45 micron filters used differ greatly from reverse osmosis membranes with respect to pore size, filtration characteristics and filtration rates which are from 100 to 1 000 times higher than in reverse osmosis membranes. Perhaps the most significant difference is the totally different membrane characteristics of the Millipore filter which only retains particulates and larger colloids as compared to the membranes which retain essentially all colloids and dissolved organics with a molecular mass of greater than about 150 to 200.

3.12

Winfield (1979) studied the effect of dissolved organics on the fouling rate of membranes and found a good correlation between ultraviolet absorbance at 275 nm and the rate of membrane flux decline. He concluded that although colloidal material plays a role in restricting water flux through a membrane, dissolved organic material appears to be the rate determining factor.

In an attempt to develop a test which would more closely simulate flow conditions in reverse osmosis modules Reed and Belfort (1982) developed a "simulated flow cell". The flow cell is a circular unit of 78 mm diameter designed to operate with a 47 mm irradiated polycarbonate membrane with characteristic pore diameters of 0,1 to 1,0 micron under a pressure of 210 kPa. Flow is tangentially across the membrane and can be varied from a Reynolds number of zero to approximately 6 000, thus simulating flow conditions at a reverse osmosis membrane.

The simulated flow cell was compared to non-flow type cells used to determine plugging indices. It was found that both types of cells produced similar results when operated under the same (non-flow) conditions. However, the advantage of the flow cell lies in the fact that different cross-flow velocities can be simulated and the rate of fouling determined under these different conditions. Except for these initial studies by Reed and Belfort (1982) no further reports or studies could be found in the literature.

From the above it is evident that existing fouling tests can at best only give a qualitative indication of the membrane fouling characteristics of a feedwater. Pilot or small-scale tests using actual membranes and modules are still the only means of obtaining information for full-scale operation.

It was nevertheless decided to set a target Plugging Index value of 50% for the quality of the feed water to the membranes and to reconsider this value in the light of actual results from the plant. It was further also decided to do comprehensive feed water characterization in terms of available fouling indices and organic parameters and to attempt to correlate these parameters with actual fouling of the membranes.

3.2.4.2 Pretreatment systems

In order to produce feed water with a Plugging Index of less than 50%, extensive pretreatment would be required. Basically two different pretreatment systems were considered, i.e. chemical coagulation-clarification-filtration, and ultrafiltration.

Extensive pretreatment is required to remove potential membrane foulants including dissolved and colloidal organic material such as humic and fulvic material, inorganic compounds that may precipitate or form scale on the membranes, bacteria that may attach to the membranes and degrade and block membranes (Argo and Ridgway, 1982; Ridgway et al., 1984) and other foulants such as oils and greases and corrosion products.

An extensive pretreatment system is discussed by Davis et al. (1981) who concluded that flux decline could be controlled more effectively by extensive pretreatment in a tubular cellulose acetate membrane system. Argo (1979) on the other hand concluded that in spite of a very high degree of pretreatment at Water Factory 21 including lime clarification, multi-media filtration and activated carbon adsorption, membrane fluxes had decreased by about 20%

3.14

after 12 000 hours of operation of the cellulose acetate spiral wound membranes. Analysis of the fouling material seemed to indicate that fouling was caused by humic material not removed from the feedwater. However, subsequent analysis and pilot plant research indicated that the fouling material was mainly viable and dead bacterial cells accumulated in the spiral wound modules on the membrane surface (Argo, 1982). The result of further pilot plant research in which lime clarified effluent without activated carbon treatment was treated directly in a reverse osmosis module confirmed earlier findings that the main foulant was not dissolved organic material (humic and fulvic acids) but rather bacterial cells. This led to the elimination of carbon treatment from the pretreatment system, because the carbon columns are excellent breeding media for bacteria as confirmed by bacterial counts in the effluent from these columns (McCarty et al., 1980).

This does, however, not mean that humic material does not foul reverse osmosis membranes. In many other studies on surface waters with relatively low bacterial counts substantial fouling of membranes was experienced (Schippers et al., 1980; Petersen et al., 1980; Leger, 1984).

Conventional water treatment processes, i.e. chemical clarification with lime, alum or iron salts e.g. ferric chloride, followed by settling/flotation and filtration are fairly successful in removing colloidal material but not dissolved organics. Fouling will therefore still occur to some extent and a membrane cleaning program will therefore always be necessary. On the other hand activated carbon treatment is effective in removing dissolved organics which may cause fouling but the carbon columns act as breeding ground for bacteria which may cause severe membrane fouling.

3.15

Care should be taken when employing chemical clarification that the reaction takes place under optimum conditions to ensure quantitative precipitation of the added chemicals. Residual iron or aluminium, especially in colloidal form, may cause severe fouling of membranes. This also applies to the use of polyelectrolytes which can cause severe fouling even in very low concentrations (Schippers et al., 1980).

Since reverse osmosis membranes are fouled by colloidal organics and dissolved organics of relatively large molecular mass in the feed water, it is reasonable to postulate that ultrafiltration should produce a reverse osmosis feedwater with a very low fouling tendency by removing these organics from the feed water.

Ultrafiltration, being a pressure driven membrane process, suffers from much the same membrane fouling problems and therefore flux reduction problems that reverse osmosis is prone to. However, ultrafiltration membranes, notably polysulphone, can tolerate very harsh cleaning regimes including high temperatures, low and high pH and many chemical cleaning agents. Much more effective cleaning of ultrafiltration membranes is therefore possible than of reverse osmosis membranes.

A number of studies have been reported in the literature on ultrafiltration pretreatment of reverse osmosis feedwater in different applications, including sea-water desalination (Hayward and Choate, 1982), industrial effluents (Matz et al., 1978) and sewage effluents (Dewalle and Chian, 1978; Argo, 1979; Petersen et al., 1980).

The findings from these studies are that ultrafiltration is only partially successful in removing organic material which causes fouling and plugging of reverse osmosis membranes. Further, that the ultrafiltration membranes themselves get fouled by organics in water and fluxes therefore decline rapidly.

In view of the relatively large capital requirement for an ultrafiltration plant, the high energy consumption and the limited success in preventing fouling of reverse osmosis membranes, ultrafiltration does not appear to be a viable method of pretreatment in the reclamation of secondary sewage effluent by reverse osmosis. It was therefore decided to base the pretreatment system on chemical clarification and multi-media filtration.

Pretreatment studies were initiated on bench-scale to determine optimum coagulation and flocculation conditions. A series of tests using ferric chloride at different dosages and at different pH values and with different flocculation aids were conducted. Findings from these tests can be summarized as follows :

- Higher coagulant doses and lower coagulation pH levels result in better MFI and UV Absorbance values.
- Increases in residual Fe present in the filtrate occur at pH values below 6,5, which places a lower limit on the usable pH range.
- Addition of bentonite as a coagulation aid has little value in the bench scale tests.

3.17

- Addition of a polyelectrolyte (a cationic polyelectrolyte in this instance) does appear to have a beneficial effect, mainly regarding better floc formation.
- Although the optimum coagulant dosage and pH could not be established by these bench tests, general trends for these parameters are shown by the results in Tables A1 - A10, Appendix A.

Figures A1 to A4 Appendix A show graphically the performance of the pretreatment plant with respect to Modified Fouling Index, Filtration Index, Turbidity and Ultraviolet Adsorbance at 275 nm. Figure A5 shows the pretreatment plant design.

The results from the bench-scale coagulation/flocculation studies were used as a basis for the pilot-scale pretreatment tests. Although formal optimization studies were not performed on the individual processes the effect of variables such as coagulant dose, coagulant pH, polyelectrolyte addition, velocity gradient in flocculator and recycle ratio of saturated feed to the dissolved air flotation unit were all investigated. Using the information gained from these tests, two extended runs were performed to evaluate the complete pretreatment system before coupling it to the RO units. The emphasis during these tests was to ensure that the prescribed membrane fouling criteria were met under continuous operation, i.e. the water produced had to have a plugging index of less than 50% or an MFI value of less than 2. At the same time the reliability of the process and the length of the filter runs could be established.

3.3 SUMMARY OF RESULTS

3.3.1 Standardization tests

Before pretreated feedwater was fed to the reverse osmosis systems two series of standardization tests were conducted. Firstly, an extended run of 650 hours was carried out on acidified tap water (pH 6,5) to ensure that the membrane compaction rate had stabilized. A very low rate of flux decline occurred over this period giving a value of $m = -0,01036$, from $\log J_v = \log J_{v0} - m \log t$

where J_v = water flux at time t

J_{v0} = water flux at start of test

m = slope of line of $\log J_v$ vs. $\log t$.

The mean salt rejection over this period was 91,5% and the mean recovery was 74,6%.

Summaries of all the pilot plant results are given in Tables A1 to A12 and Figures A1 to A12, Appendix A.

After the initial compaction run on tap water a standardization run was conducted on 2 000 mg/ℓ sodium chloride. The results of this test are given in Tables 3.1 and 3.2 for the cellulose acetate pilot plant and composite membrane module respectively. Table 3.3 shows the performance of individual modules in the pilot plant during the standardization tests. The salt rejection attained by the cellulose acetate unit on the 2 000 mg/ℓ NaCl solution was fairly low, at 82,9%, but as this was calculated to be equivalent to a mean membrane rejection of over 91% the results were considered to be satisfactory. The corrected flux attained was in excess of the manufacturers specification of 780 ℓ/m².d for new unfouled membranes. The third column of Table 3.1, shows the last standardization test carried out on the unit, which is discussed in more detail in Section 3.4.

TABLE 3.1 CELLULOSE ACETATE UNIT - STANDARDIZATION TESTS ON
2 000 mg/l NaCl SOLUTION

		Initial Test (16/5/83 to 17/5/83)	After Replacing 3 modules (19/5/83)	Latest Test (21/11/83)
Module Inlet Pressure	kPa	3830	3830	4119
Module Outlet Pressure	kPa	2120	2130	1920
Feed Temperature	°C	26,4	22,1	24,7
Plant Recovery	%	80,59	78,03	80,40
Actual Flux	$\text{L.m}^{-2}.\text{d}^{-1}$	755	880	844
Corrected Flux (20°C, 4000 kPa)	$\text{L.m}^{-2}.\text{d}^{-1}$	795	803	814
Rejection by Plant	%	81,60	82,91	84,67
Mean Membrane Rejection	%	90,96	91,22	92,27

TABLE 3.2 COMPOSITE MEMBRANE MODULE STANDARDIZATION TESTS
ON 2 000 mg/l NaCl SOLUTION

		Initial Test on 16/6/83	Latest Test on 13/1/84
Module Inlet Pressure	kPa	4137	4137
Module Outlet Pressure	kPa	3313	3343
Feed Temperature	°C	19	27
Plant Recovery	%	15,61	18,31
Actual Flux	$\text{L.m}^{-2}.\text{d}^{-1}$	1061	1620
Corrected Flux (20°C, 4000 kPa)	$\text{L.m}^{-2}.\text{d}^{-1}$	937	1219
Rejection by Plant	%	89,82	93,54
Mean Membrane Rejection	%	89,65	93,68

TABLE 3.3 COMPARISON OF INDIVIDUAL MODULE PERFORMANCES DURING STANDARDISATION TESTS

Module Number	Rejection Percentage		Corrected Flux ($\mu\text{m}^{-2}\text{d}^{-1}$)	
	19/05/83	30/11/83	19/05/83	30/11/83
1	91,5	89,6	762	721
2	93,2	90,9	864	820
3	92,3	89,3	814	750
4	94,0	90,5	867	782
5	91,6	90,0	964	923
6	92,6	88,9	1062	935
7	95,2	93,8	760	708
8	95,3	93,5	752	684
9	91,6	90,4	892	911
10	92,1	86,7	915	830
11	92,1	89,8	899	853
12	94,8	93,8	708	658
13	93,1	80,4	972	995
14	91,4	81,7	861	969
15	90,1	79,9	812	914
16	92,3	86,9	825	968
17	93,8	78,6	1004	1012
18	90,0	76,8	895	896
19	92,4	84,1	861	1009
20	91,2	77,8	992	1154
21	89,5	73,2	722	1329
22	88,8	71,2	693	1204
23	90,3	71,0	733	1169
24	89,3	67,1	716	987
25	93,5	83,1	631	781
26	89,7	61,1	805	1016
27	90,6	73,2	773	737
28	90,7	71,0	854	813
29	92,2	70,9	934	836
30	91,8	68,5	929	780

3.3.2 Water reclamation test run (cellulose acetate unit)

The unit was on line for a total of 4 075 hours during the test period which lasted for just over 6 months (4 596 hours). The unit was operated at an inlet pressure of between 3 200 to 4 030 kPa with feed water temperature which varied between 14 and 26°C and a pH range of 5,1 to 6,2 with an average of 5,8.

Up to 2 172 hours the unit operated as expected but subsequently a progressive loss in rejection was detected. At 2 920 hours a module survey was conducted which showed that the last four modules in the third stage showed a definite loss of rejection. These modules were removed giving a configuration of 3x4, 2x4 and 6x1 modules in a 26 module array with the same output as initially. At 4 215 hours the performance of the plant had again deteriorated and after a further module survey the entire third stage was removed. The unit, then operating with a 3x4, 2x4 array operated satisfactorily, showing very little loss of output (based on plant design) and improved rejection.

Tables 3.4 and 3.5 show the performance of individual modules during module surveys, while Figure 3.2 shows the corrected water flux and Figure 3.3 the salt passage during the period of operation respectively.

3.3.3 Summary of results from the composite membrane module

Since this unit consisted of only one module operating in an once through mode, very low water recoveries were possible. In order to simulate conditions that would be experienced in a full-scale plant the feed water to this plant was made up of a mixture of reject from the pilot plant and pretreated feed water. In this way it was attempted to simulate performance of a module towards the middle of a hypothetical full-scale plant.

TABLE 3.4 REJECTIONS DURING MODULE SURVEYS - WITH BAKKE
RO OPERATING ON PRETREATED FEED

Date	14/10/83	02/11/83	14/11/83	22/11/83	10/12/83
Module Config.	12-8-6	12-8-6	12-8-6	12-8-6	12-8
Mod. No.	1	2	3	4	5
1	93,8	94,9	94,6	94,4	94,5
2	94,6	95,4	95,2	95,1	95,1
3	93,9	94,8	94,6	94,4	94,5
4	94,8	95,6	95,3	95,1	95,0
5	94,4	95,2	94,8	94,6	94,6
6	94,0	94,9	94,8	94,2	94,2
7	95,7	96,4	96,5	96,6	95,9
8	96,1	96,6	96,6	96,5	96,5
9	94,4	95,3	95,0	94,7	94,7
10	93,9	94,6	94,6	94,2	93,5
11	94,4	95,3	94,9	94,6	94,8
12	96,1	96,7	96,6	96,6	96,8
13	90,1	91,3	91,8	90,3	89,3
14	92,6	92,5	91,8	90,3	89,9
15	91,9	92,1	91,2	89,8	89,9
16	94,2	94,5	94,0	93,4	93,6
17	92,2	92,0	91,3	89,4	89,0
18	90,6	90,6	90,1	88,2	88,3
19	93,5	93,7	93,1	92,0	92,0
20	91,5	91,4	90,2	88,5	95,5*
21	91,9	91,3	89,7	86,9	
22	91,6	91,0	89,2	86,4	
23	92,1	91,3	89,6	86,6	
24	91,0	90,0	88,1	85,1	
25	95,4	95,3	94,8	93,6	
26	90,2	88,7	86,8	83,1	
Mean (for unit)	87,0	86,3	85,3	82,3	87,4

* Module 25 placed in this position

TABLE 3.5 CORRECTED FLUXES DURING MODULE SURVEYS - WITH
BAKKE RO OPERATING ON PRETREATED FEED

Date	14/10/83	02/11/83	14/11/83	22/11/83	29/12/83
Module Config.	12-8-6	12-8-6	12-8-6	12-8-6	12-8
Mod. No.	$\text{L.m}^{-2}.\text{d}^{-1}$ at 20°C and 4000 kPa				
1	764	802	780	783	785
2	867	909	890	913	890
3	820	850	831	844	846
4	865	887	876	889	867
5	944	988	972	995	971
6	980	1017	1009	1014	994
7	780	807	789	790	803
8	750	786	771	783	790
9	947	982	954	999	989
10	932	910	885	962	785
11	897	941	919	945	948
12	728	755	746	754	764
13	1063	1148	1112	1152	1008
14	980	1082	1060	1107	965
15	872	972	946	999	851
16	983	1070	1050	1090	982
17	1061	1159	1131	1183	1005
18	936	1005	976	1005	917
19	960	1087	1067	1108	903
20	1124	1219	1146	1232	909*
21	1010	1439	1347	1432	
22	919	1300	1230	1308	
23	934	1270	1257	1315	
24	783	1100	1036	1071	
25	687	951	914	935	
26	813	1186	1119	1161	
Mean (for unit)	865	993	972	994	876

* Module 25 placed in this position

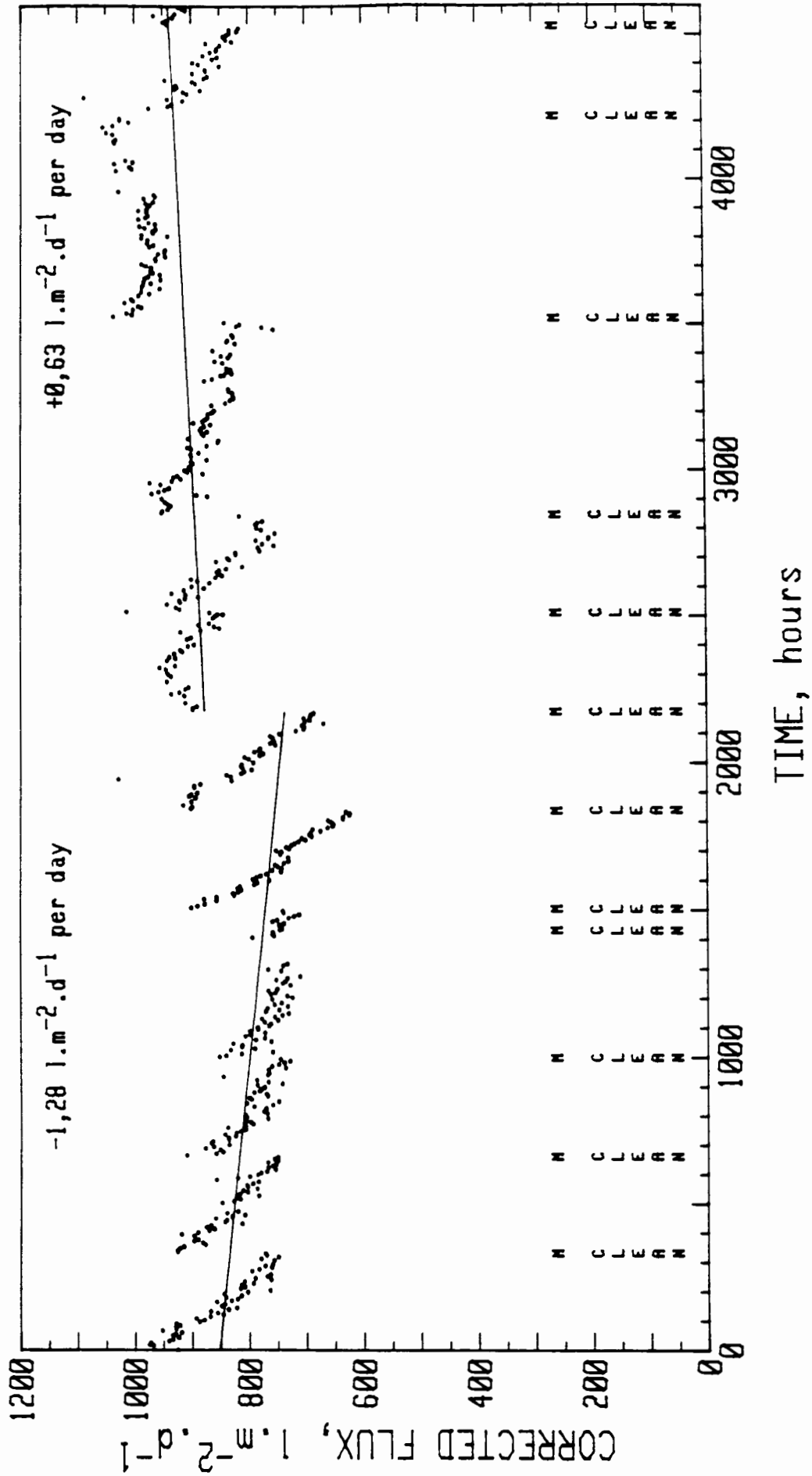


FIGURE 3.2 CORRECTED WATER FLUX OF MODULES IN PILOT PLANT

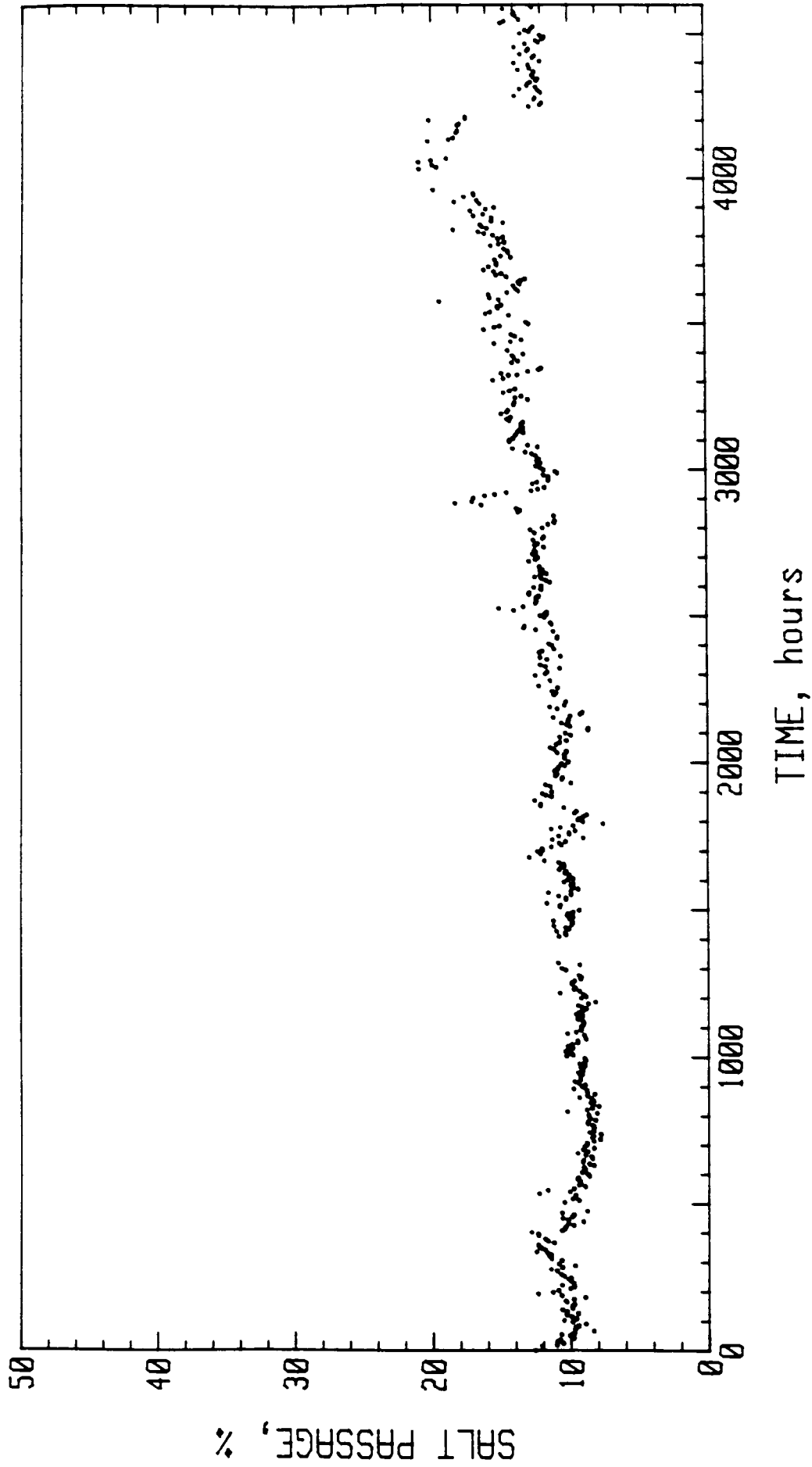


FIGURE 3.3 PERCENTAGE SALT PASSAGE OF MODULES IN PILOT PLANT

The initial flux of the standardization test i.e. 987 $\ell/m^2.d$ could not be achieved in the water reclamation test and the flux actually dropped very rapidly over the first 130 hours to 760 $\ell/m^2.d$. Initial attempts to wash the membranes were not successful and the flux dropped to 450 $\ell/m^2.d$ at 1800 hours. At this stage sponge ball cleaning was introduced without any marked degree of success. There were, however, indications that the flux decline was flattening out. From 2 500 hours onwards there was a dramatic increase in membrane flux, and fluxes increased after every wash. At about 3 500 hours the flux had risen to above its initial level and was still rising when the project was terminated. Figures 3.4 and 3.5 show the corrected water flux and salt passage respectively for the period of operation. The salt passage had been extremely low during the first 3 800 hours of operation and on average had increased at a rate of 0,002% per day from initial values of around 0,8%. However, coinciding with the steady increase in flux, the salt passage increased progressively after about 3 800 hours, but was still only about 2% when the test was stopped.

3.4 DISCUSSION OF RESULTS

The discussion in this section focusses on the following aspects (i) membrane flux; (ii) membrane rejection characteristics; (iii) reclaimed water quality.

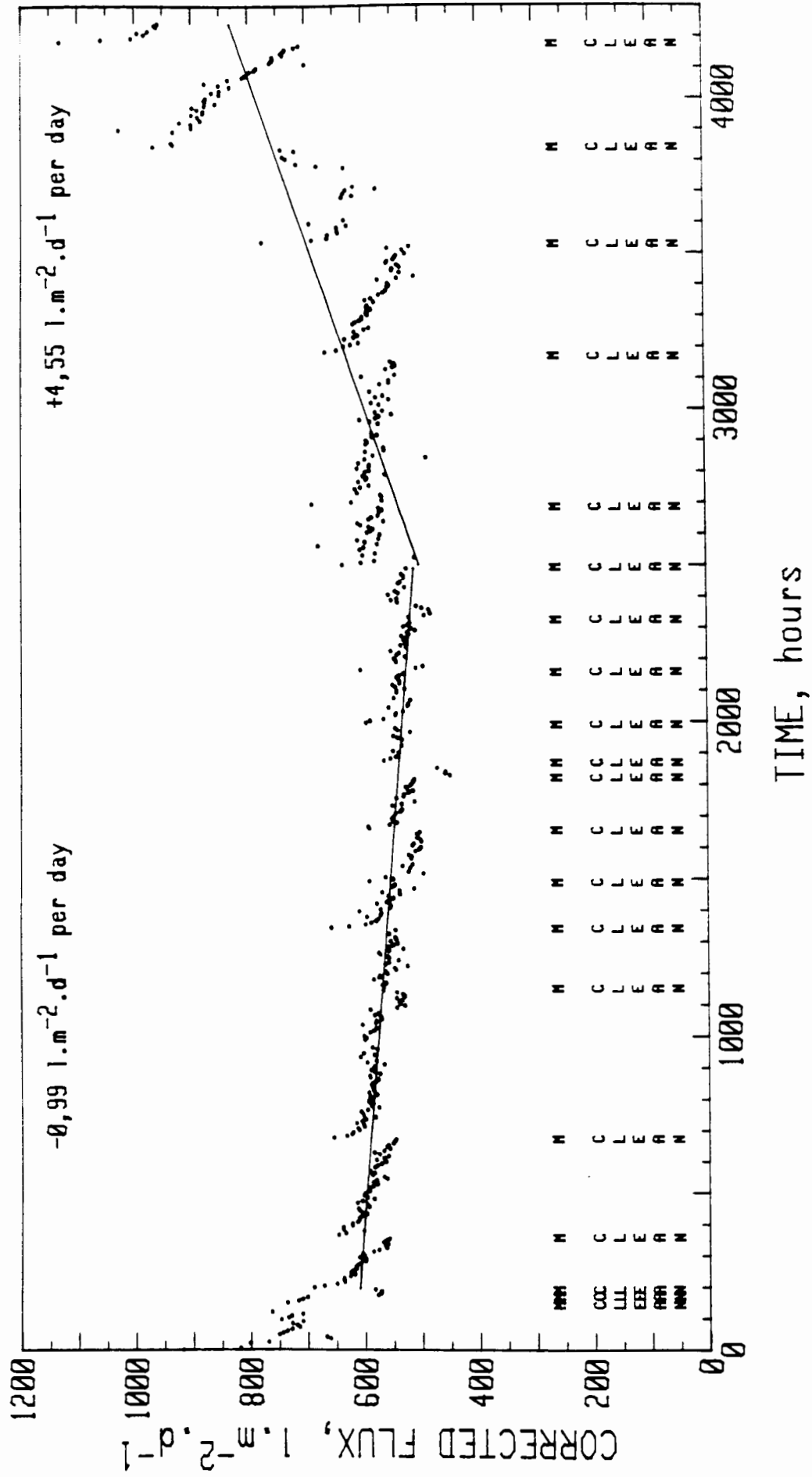


FIGURE 3.4 CORRECTED WATER FLUX OF COMPOSITE MEMBRANE MODULE

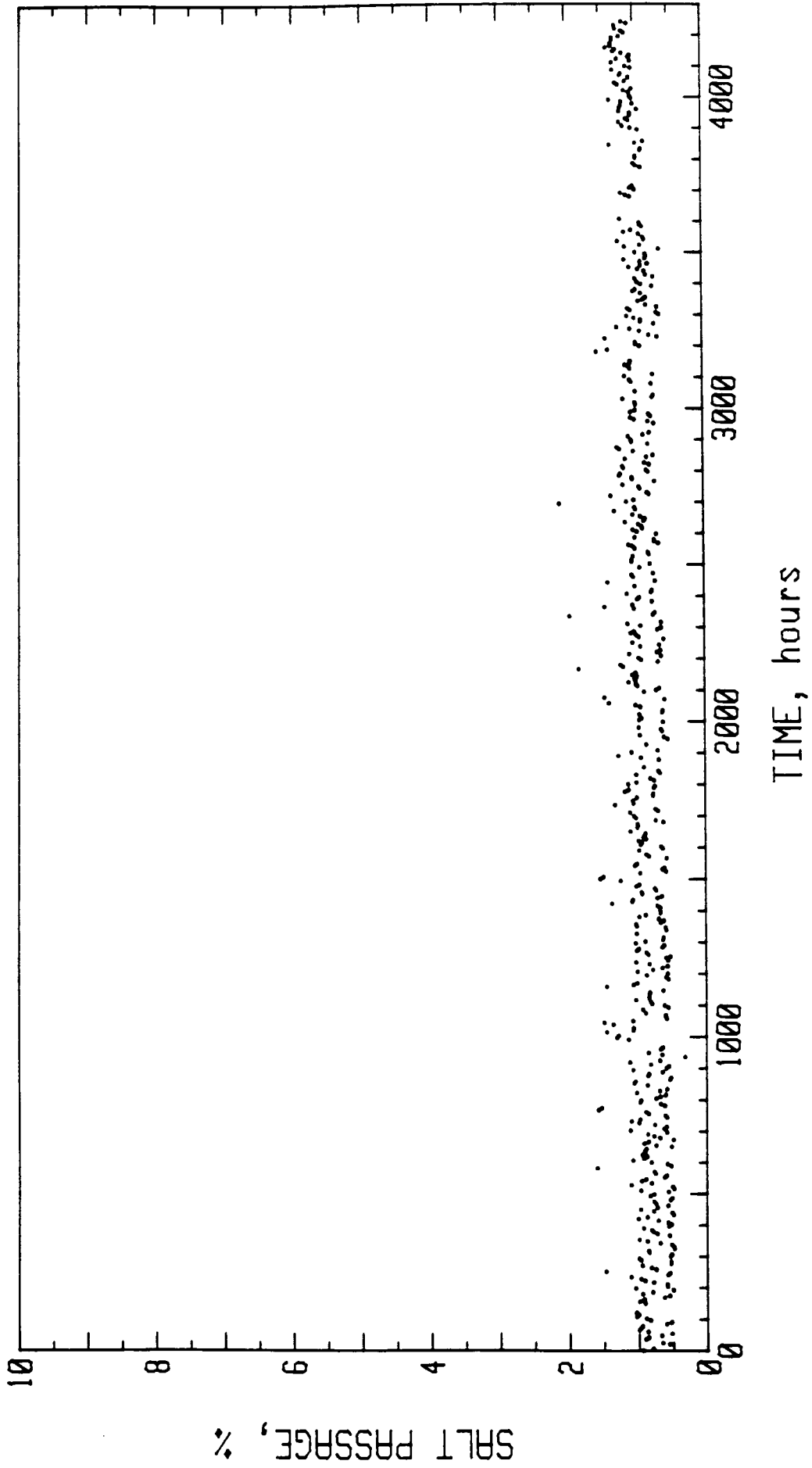


FIGURE 3.5 PERCENTAGE SALT PASSAGE OF COMPOSITE MEMBRANE MODULE

3.4.1 Membrane flux

One of the main objectives of these studies was to determine the rate of flux decline due to membrane fouling and to develop cleaning and washing procedures to maintain fluxes at economically acceptable levels. The pretreatment studies were successful in that the Fouling Index and Modified Fouling Index could be reduced substantially by the pretreatment system employed. However, no significant correlation could be found between any of the indices determined and actual fouling of the membranes. The Modified Fouling Index and the Plugging Index are both fairly sensitive to changes in water quality while turbidity and ultraviolet absorbance are less sensitive to variations in water quality with respect to membrane fouling.

An important point relating to pretreatment is that, in spite of the very good quality feedwater produced by the pretreatment system, the quality deteriorates rapidly with passage across the membranes so that the brine from one stage which forms the feed to the next is of a very much poorer quality than the original feedwater. The effect therefore is that, especially the third stage received a poor quality water relative to the feed of the first stage and to a lesser extent also of the second stage. Further, any residual pretreatment chemicals such as residual iron, polyelectrolytes, chlorine and other potentially harmful material in the feedwater become concentrated down the line. This is also true for cleaning agents including acids, bases, detergents and chelating agents which are present at higher concentrations in the second and third stages of a tapered reclamation plant.

It can therefore be concluded that the pretreatment system employed is effective in improving feedwater quality with respect to the Fouling Index factor and the Modified Fouling Index. The first stage modules in the tapered plant therefore see feedwater of a relatively good quality but the quality deteriorates with passage across the membranes (to the extent that these indices cannot be measured on brine from the first stage because the test membrane filter gets plugged completely). The membranes in the third stage are fed continuously with feedwater of a relatively poor quality and should therefore get fouled to a much greater extent and therefore require more drastic cleaning procedures more often and for longer periods to restore fluxes than membranes in the first and second stages. The advantage of having a third stage to achieve a higher water recovery may be cancelled to a certain extent due to the problems discussed above.

Results from the membrane cleaning exercises were rather inconclusive. Figures 3.2 and 3.4, show the corrected flux vs. time for the two units. In both cases a distinct break in the curves occurs with fluxes increasing for some unexplained reason after about 2 500 hours. Since these flux increases were accompanied by increases in salt passage it seems obvious that the membranes must have suffered some form of damage.

It should be pointed out that the pilot plants were operated at relatively high pressures (about 4 000 kPa) and at relatively high actual flux levels, viz. in the order of 500 to 700 $\ell/m^2.d.$ High flux levels give rise to increased concentration polarization and an increased tendency to fouling. However, in tubular systems operating at high linear velocities and incorporating sponge ball cleaning and flow reversal the effects of concentration polarization are countered to some extent.

The effects of different cleaning procedures on membrane flux are shown in Tables A11 and A12, Appendix A. These are average values for all the membranes in the plants as a whole and do not give an indication of the performance of individual modules or sections of the plant. Some information on individual module performance may be gleaned from modular surveys which are reported in Table 3.4 and from module tests during standardization, Table 3.3. The corrected flux values clearly show the extent to which fluxes in the second and third stages of the plant have increased. The only conclusion that can be drawn is that these modules have been damaged resulting in the flux increases. A more detailed discussion is given in the next section.

It is evident from the results given that sponge balls and flow reversal are only effective in preventing excessive fouling of membranes between chemical cleanings. These physical cleaning methods alone cannot prevent fluxes from declining excessively. Chemical cleaning of a particular membrane is successful only with specific cleaning agents. Conditions must be carefully controlled during chemical cleaning otherwise membranes and/or support materials may be damaged resulting in increased salt passage.

3.4.2 Membrane rejection characteristics

Although it is not essential in water reclamation applications to have very high rejecting membranes in order to produce water of acceptable quality (500 mg/ℓ total dissolved solids) there are a number of factors to be considered. Firstly, when there is a downward trend in rejection characteristics, membrane life expectancy may be reduced, having serious economic implications. Secondly,

water quality with respect to dissolved organic material is much better with very high rejecting membranes compared to membranes with lower salt rejecting characteristics, and thirdly in applications where blending of reverse osmosis reclaimed water with conventionally reclaimed water is considered to produce water of acceptable quality, a smaller proportion of water from a high rejecting membrane will be required to produce water of the required total dissolved solids content than with a poorer rejecting membrane.

When an increase in membrane flux is accompanied by a lower salt rejection it can usually be assumed that irreversible damage has occurred. The pilot plant showed a marked increase in salt passage after membrane flux had started to increase, while the composite module showed a relatively small but significant increase in salt passage towards the end of the pilot plant trials.

The module surveys of the pilot plant, Tables 3.4 and 3.5 show that the largest increases in both membrane flux and salt passage occurred in the modules of the third stage of the plant and that the modules in the first stage and to a lesser degree in the second stage were still performing quite well.

The deterioration in salt rejection characteristics of the membranes in the pilot plant has important implications for further research in this field and consequently an intensive study was launched to identify possible causes for this deterioration. The following aspects were investigated :

- (i) The effect of extended exposure to cleaning chemicals on membrane performance was investigated by the Institute for Polymer Science, University of Stellenbosch.

From the results (Tables A13 to A18, Appendix A) it can be concluded that under the conditions chosen for the tests, the membrane cleaning chemicals had no adverse effects on the performance of new membranes similar to those that had been used in the pilot plant tests. It must be pointed out though, that these tests were of relatively short duration and that they were conducted using clean membranes and clean water without chlorine or other (residual pretreatment) chemicals.

- (ii) The effect of exposure to higher levels of FeCl_3 and free chlorine for short periods of time. This study was conducted by the National Institute for Water Research of the CSIR on two modules removed from the pilot plant; one that showed a marked loss of rejection and the other relatively unaffected.

From the results (Table A19 Appendix A) no sign of permanent deterioration of the membranes is apparent.

Here again, it should be remarked that the test was of short duration and conditions during this test and the tests under (i) above are entirely different from operational conditions where long-term exposure to FeCl_3 and Cl_2 is interrupted by regular cleaning cycles which may have a completely different effect on the membranes. Even very small quantities of residual iron from the pretreatment system will get concentrated at the membrane surface where it may affect the membrane, such as by causing localised increases in pH which may cause damage to the membrane.

- (iii) In addition to these tests various analyses were conducted in an attempt to explain what had happened to the membranes.

A membrane consultant concluded that no physical damage was caused either by bacteria or sponge balls or by pH hydrolysis. These conclusions were based on physical examination and on the solubility of the membranes in acetone. The most probable cause of the damage according to the consultant is "enzyme hydrolysis", which has been widely observed with cellulose acetate membranes and is thought to be caused by a cellulose digesting enzyme which attacks the cellulose substructure of the cellulose acetate. Chlorine appears to be specific to the problem - probably by either activating the enzyme or deactivating a sequestering agent. Tests by the Institute for Polymer Science, University of Stellenbosch on new and used membranes failed to show any viscosity differences or changes in molecular mass distribution which would have been indicative of enzyme hydrolysis.

- (iv) The National Institute for Water Research of the CSIR conducted microscopic examination, energy dispersive analysis (EDAX), stereo microscopic examination and infra-red spectrophotometric scans of new and used membranes and on fouling material in order to gain some insight into the causes of loss of performance of the membranes.

Conclusions from these tests were that :

- (i) there were large numbers of bacteria present in the fouling material on the membranes;
 - (ii) approximately 30% of the fouling material was of organic origin;
 - (iii) the fouling substance had a particulate structure with particle sizes varying from 0,1 to 1 micron;
 - (iv) the major inorganic foulant was iron followed by phosphorus;
 - (v) there were large numbers of bubbles in the membrane; and
 - (vi) the new and used membranes contained only pure cellulose acetate indicating that no degradation products are present. (These products are, however, water soluble and may have been washed away).
- (v) The Department of Chemical Engineering, University of Cape Town conducted electron microscope studies on the membranes and foulant layers. They concluded that, although some cracks were visible in sections of the membrane, it was not possible to determine what caused the cracks or when they were formed. No conclusive evidence on possible membrane degradation or cause could be derived from these studies.

In summary it can be stated that no conclusive evidence or single cause for the membrane degradation could be found. The most likely explanation is that membrane damage was caused by a combination of factors and that the effects of residual pretreatment chemicals (Fe and Cl₂) together with the effects of chemical cleaning agents which were accentuated by the tapered plant configuration may all have contributed to the damage - although this has not been proved conclusively.

3.4.3 Reclaimed water quality

The results of chemical and bacteriological analysis on reclaimed water from the pilot plant (Tables A20 - A25, Appendix A) show that reclaimed water of a very good quality was produced. Inorganic species were consistently reduced to low levels, with the exception of oxidized nitrogen compounds which are not effectively rejected by the cellulose acetate membranes. Residual organic substances as determined by chemical oxygen demand (COD), total organic carbon (TOC) and ultraviolet absorbance are well rejected by the membranes (in the order of 90% rejection). Lower molecular mass, more volatile compounds such as the trihalomethanes or volatile organohalogens, including chloroform are poorly rejected. However, being volatile these compounds are easily removed from water by air stripping and since removal of dissolved gases is usually required after reverse osmosis in order to stabilize the water these volatile compounds will therefore also be removed to low levels.

It was found that precursor material for the formation of trihalomethanes was not rejected by either the cellulose acetate or the thin film composite membranes. Since it is generally accepted that precursor material consists mainly of humic and fulvic compounds with relatively high molecular masses, this material should be well rejected by both membranes. The fact that this was not the case appears to be an anomaly for which no apparent reason can be given. A summary of these results is given in Table 3.6

Table 3.6 : Chemical analysis of raw feed water, pretreated feed water and permeates

Date	Raw Feed			Pretreated Feed		Bakke RO permeate			PCI RO		
	TOC mg/ℓ	TOHP μg/ℓ	UV Abs. 275 nm	TOC mg/ℓ	UV Abs. 275 nm	TOC mg/ℓ	TOHP μg/ℓ	UV Abs. 275 nm	TOC mg/ℓ	TOHP μg/ℓ	UV Abs. 275 nm
1983											
20/09	9,8	2642	0,275	5,8	0,142	0,8	5656	0,054	0,2	3832	-
27/09	11,0	1915	0,275	6,6	0,154	<1,0	1843	-	<1,0	1533	-
04/10	9,4	1533	0,237	5,8	0,100	1,0	1013	0,010	1,0	782	0,010
12/10	10,8	1634	-	-	-	3,8	1065	0,020	1,6	792	0,010
18/10	8,8	2105	0,239	5,4	0,144	1,0	2030	0,090	1,2	1585	0,010
01/11	16,0	1000	-	-	-	5,0	1000	0,080	3,2	1000	0,010
08/11	10,4	1736	0,290	5,8	0,139	1,8	2102	0,020	1,0	2504	0,010
22/11	9,8	> 1000	0,265	5,0	0,118	0,4	> 1000	0,030	0,6	> 1000	0,010
06/12	10,8	868	0,268	6,4	0,131	1,6	435	0,040	1,6	522	0,020
13/12	9,8	> 1000	0,268	6,2	0,137	<1,0	655	-	2,0	314	-

The bacteriological results from the pilot plant study show very good rejection by the membranes although some organisms are present in the permeate. In view of the size of these organisms they should be rejected completely by the membranes but they do penetrate the membranes through imperfections and leaks. Final chlorination in a water reclamation plant should ensure complete assurance against any harmful organisms that may penetrate the membranes.

3.5 SUMMARY OF THE PORT ELIZABETH PROJECT

The Port Elizabeth study was conducted by the Municipality of Port Elizabeth in collaboration with Bintech (Pty) Ltd. (Vail and Barnard, 1986). As is pointed out in Section 3.2 this study was designed as a control to the Bellville study. Both pilot plants used similar membranes from the same manufacturer and had basically the same objectives. The main differences between the two projects were :

- (i) The Port Elizabeth pilot plant consisted of a single pass system arranged in two parallel rows of 16 modules each (Figure 3.6), compared to the tapered configuration of the Bellville pilot plant.
- (ii) The feedwater to the Port Elizabeth pilot plant was activated sludge effluent filtered through an upflow rapid sand filter as only further treatment, compared to the extensive pretreatment of the Bellville feed water.

The unit has operated for more than 10 000 hours at the time of reporting (Vail and Barnard, 1986) and since then a further 5 000 hours have been accumulated (Vail, 1986).

One of the main objectives of this project was to study the effectiveness of membrane cleaning procedures including module flow reversal, sponge ball cleaning and chemical cleaning. Results show that these procedures were very effective and that only a relatively small flux drop occurred over the operating period. The average peak standard flux (measured immediately after each chemical cleaning) was $646 \text{ l/m}^2 \cdot \text{d}$ during the 300 to 2 000 hour period.

Figure 3.7 shows a plot of the peak standard flux over the first 10 000 hours of operation as well as plots of % rejection, volume recovery and washing procedures. This study also shows that chemical cleaning on a regular basis is necessary in addition to flow reversal and sponge ball cleaning to maintain fluxes at acceptable levels. Various wash solutions have been tested and it appears that both enzyme and detergent components are necessary in the wash solutions, while it is unlikely that a chelating agent or citric acid are required for this particular feed water.

Salt rejection stayed fairly constant for more than 9 000 hours. This was confirmed by salt rejection surveys on individual modules at regular intervals. From about 9 000 hours a gradual decline in rejection became apparent. This decline, however, levelled off at about 10 500 hours and 85% rejection coincidental with a change from alkaline to acid washing solution (Vail, 1986).

Results of chemical analyses are given in Tables A26 to A28, Appendix A.

It appears from the big difference in performance of the two pilot plants, especially with respect to membrane life, that the pretreatment in the Bellville plant may have been the main cause of the premature membrane failure in that plant. The fact that the membranes in the third stage suffered the biggest damage indicates that the concentrating effect of the tapered flow accentuated any possible harmful effects from residual chemicals or agents. In

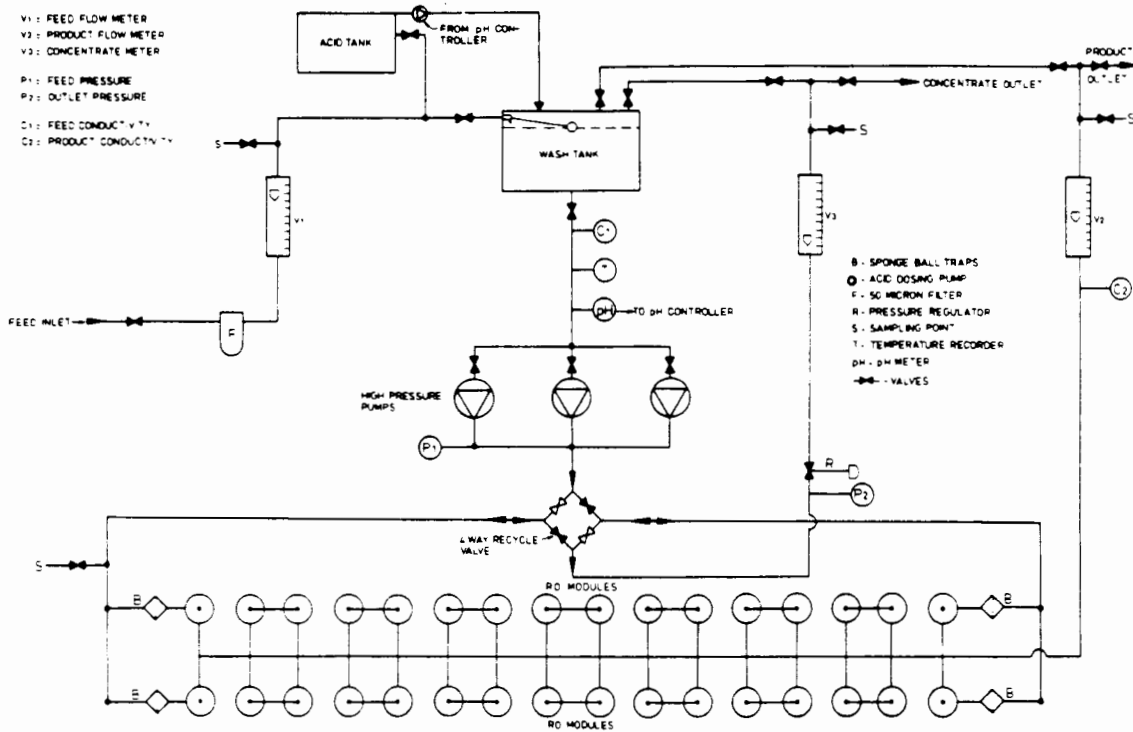


FIGURE 3.6: PORT ELIZABETH PILOT PLANT LAYOUT
(Vail and Barnard, 1986)

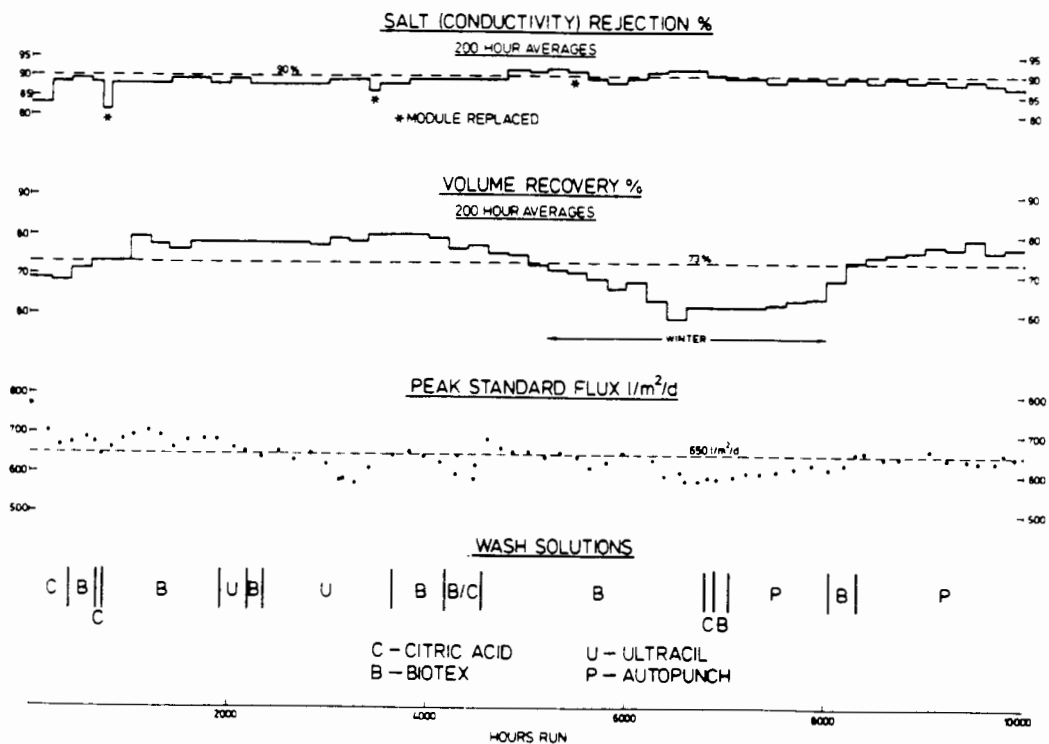


FIGURE 3.7: PORT ELIZABETH PILOT PLANT PERFORMANCE
(Vail and Barnard, 1986)

the once through Port Elizabeth plant the effect of periodic flow reversal is that the end membranes alternately received the clean feed water and the most concentrated reject flow, while in the tapered plant the third stage membranes constantly received the concentrated reject flow from the second stage in spite of flow reversal.

3.6 CONCLUSIONS

- (i) The pilot plant studies confirmed that acceptable flux levels can be maintained in tubular reverse osmosis plants treating well oxidized activated sludge effluent with and without extensive pretreatment provided both chemical and physical cleaning methods are employed.
- (ii) Chemical cleaning of membranes is essential to restore flux levels while physical cleaning by means of flow reversal and sponge balls assists in prevention of rapid membrane fouling.
- (iii) Extensive pretreatment is not necessary in a once through plant employing flow reversal, provided linear flow velocities are kept above 0,7 m/s. In a tapered flow plant advanced pretreatment is necessary in order to prevent excessive fouling of membranes in the last stage.
- (iv) The rejection characteristics of some of the membranes in the Bellville plant deteriorated prematurely due to undefined reasons. It appears that a combination of factors including (a) conditions during chemical cleaning (b) residual chemicals from pretreatment and cleaning and (c) the concentration effect of the tapered plant configuration contributed to the degradation of membranes in the last stage of the plant. the fact that the rejection characteristics of the composite membranes also deteriorated, albeit to a much smaller extent in absolute terms, also indicates that residual chemicals may be responsible for damage to the membranes.

- (v) An economically acceptable membrane life can be achieved provided that the use of chemicals (especially iron salts) is excluded or closely controlled so as to remove any residuals from the feed water to the membranes. The use of chemicals in the cleaning of membranes should also be closely controlled.

- (vi) A very good quality product water is produced in terms of bacteriological and organic quality. Post treatment will, however, be required for final disinfection and for the removal of residual small molecular mass organics.

3.7 RECOMMENDATIONS

Based on the findings of the pilot plant studies it is recommended that further research on a larger scale should be conducted in order to obtain design and operating criteria for large scale application. The design of such a plant should be based on a once through configuration incorporating sponge ball cleaning and flow reversal. Feed water should be sand filtered activated sludge effluent without any further pretreatment.

CHAPTER 4

LITERATURE AND EXPERIMENTAL STUDIES ON THE REJECTION OF DISSOLVED ORGANIC COMPOUNDS BY REVERSE OSMOSIS MEMBRANES

4.1 INTRODUCTION

It was concluded from the desk study on the rejection of contaminants by reverse osmosis membranes (Section 2.4) that mainly low molecular mass, relatively volatile organic compounds permeate reverse osmosis membranes. Some of these compounds have been identified as suspected carcinogens and their removal in water reclamation applications is therefore relevant. It was also shown in the desk study that solute rejection is determined by solute and membrane characteristics which result in different degrees of removal by different membranes. The main recommendation from the desk study is that a fundamental experimental study be undertaken on the rejection of organics by reverse osmosis membranes and that an attempt be made to develop a simple predictive model for the rejection of organics of interest.

The study described in this chapter has the following objectives :

- (i) to review existing membrane models and to identify those that can be used as simple predictive models, or to develop a new model or modify an existing model for this purpose.
- (ii) to obtain experimental data on the rejection of different solutes by different membranes in order to test and evaluate the proposed model.

4.2 REVIEW OF MEMBRANE TRANSPORT MODELS

4.2.1 Introduction

It is convenient to describe the transport characteristics of membranes i.e. solvent and solute flux and rejection of solutes in terms of membrane transport models which should enable one to calculate the relevant transport parameters and to predict the effects of operating and other variables on the performance of the membrane.

Basically there are two types of models : Those that presuppose a membrane transport mechanism (and therefore incorporate membrane properties e.g. thickness, pore size etc) and those that do not, i.e. treat the membrane as a "black box" such as the models based on the thermodynamics of non-linear irreversible processes. The physical significance and meaning of parameters and coefficients in the various models depend on the mechanism adopted for the model and on the assumptions made.

In mechanistic membrane models there are two phenomena that must be considered; viz. equilibrium phenomena and transport phenomena. In models based on thermodynamics of irreversible processes these phenomena are included in the "black box" and are accounted for by various coefficients and constants.

Equilibrium effects have to do with forces of attraction and repulsion between the membrane and solute, and membrane and solvent, and with interactions between solvent, solute and membrane. Phenomena such as solvent and solute sorption by the membrane and solubilities of solvent and solute in the membrane are important. These effects determine in part whether a particular solute will be rejected by a membrane, for example when the forces of repulsion between solute and membrane are strong. If the concentration of solute in the membrane is high as a result of strong forces of attraction the potential for a large solute flux and poor rejection is also high. If the forces of attraction are very strong the solute may be partially retained in the membrane thus slowing down the rate of permeation.

4.3

These forces, effects and interactions are somewhat similar to those encountered in and governing adsorption of solutes by active carbon. Conceptually, it should therefore be possible to describe these interactions by models used to describe adsorption by active carbon. Alternatively, if solubility of solvent and solute in the membrane is important, an approach based on solubility parameters should describe the equilibrium effects more accurately. Membrane transport is, however, not only determined by these equilibrium effects but also by transport phenomena.

Transport phenomena have to do with the transport of solvent and solute through the membrane under driving forces of pressure and concentration. For membranes in general, transmembrane transport consists of two components : a diffusive and a convective component. In continuous membranes such as liquid membranes transport is solely due to diffusion and in highly porous membranes transport is mainly convective. In microporous membranes transport may be due to both diffusion and convection while it can be expected that in very tight reverse osmosis membranes diffusive flow will predominate.

Membrane performance. The performance of a membrane is measured by the relative permeabilities of solute and solvent. The best performance is achieved with a high solvent permeability (high water flux) and very low solute permeability (high solute rejection).

Permeability or permeation is a phenomenological term which describes mass transfer through a membrane without being specific about the transport mechanism. This allows one to use the conditions of the bulk solutions on either side of the membrane rather than the actual concentrations in the membrane which are required to describe the processes of dissolution and diffusion.

4.4

Solvent permeation or water flux (J_v) is expressed in terms of volume per area per unit time as $\ell/m^2 \cdot d$ or $cm^3/cm^2 \cdot s$.

Solute permeation (J_s) is expressed in terms of mass per area per unit time as $mmol/cm^2 \cdot s$ or $mg/cm^2 \cdot s$.

Solute rejection (R) is expressed as the percentage of solute that permeates the membrane relative to the bulk feed concentration as

$$R = \frac{\text{conc in feed} - \text{conc in product}}{\text{conc in feed}} \times 100$$

In order to describe transport phenomena in a membrane in more quantitative terms it is necessary to consider the different regions and characteristics of solutions inside and outside the membrane. Consider the following case where an asymmetric membrane separates two solutions of different concentrations.

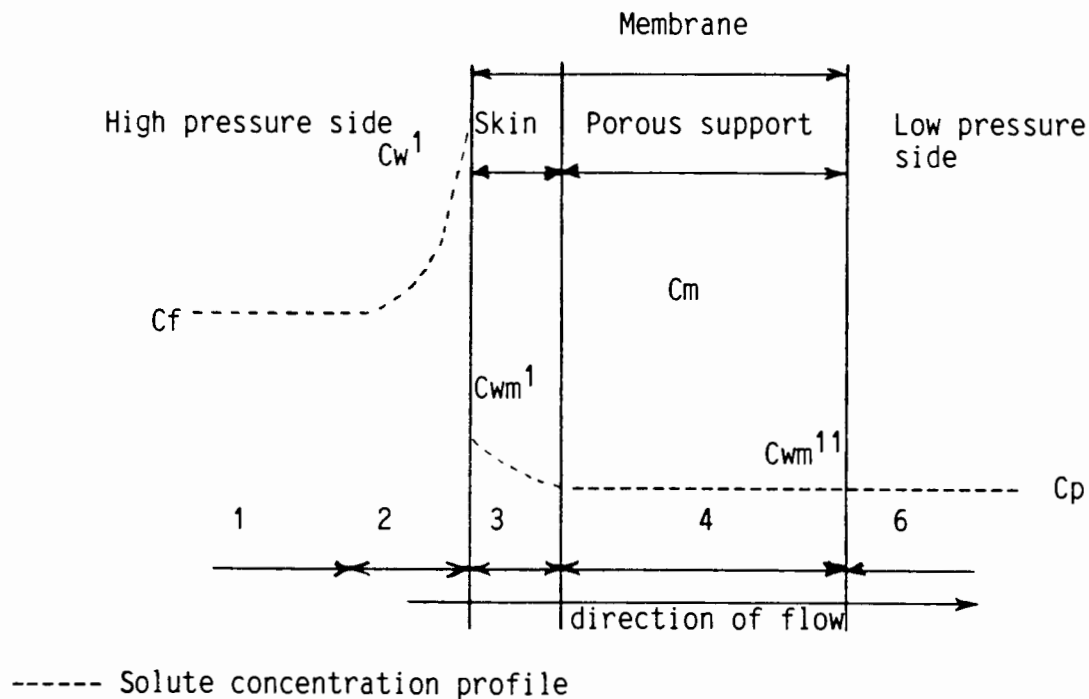


Figure 4.1. Schematic representation of membrane separating solutions of different concentrations

4.5

1. Bulk region high pressure side : The concentration of the solute in the bulk solution remains constant at C_f under steady state conditions.
2. Boundary layer high pressure side : Because solute is rejected by the membrane the solute concentration increases sharply near the membrane surface due to concentration polarization. Solute build-up is controlled by back diffusion to the bulk region.
3. Skin layer : The skin layer is very dense and effects the rejection of solute. The actual structure of the membrane whether it contains very small pores or whether it is homogenous is not known. The depiction in Figure 4.1 is according to the solution-diffusion model developed by Lonsdale et al. (1965) which states that solvent and solute dissolve in the membrane and then diffuse through through the membrane under the driving force of their respective chemical potentials. Thus, the solute concentration just inside the membrane C_{wm}^1 is much lower than at the membrane surface due to poor solubility of the solute in the membrane (one of the prerequisites for a high rejection). Solute transport in the skin is believed to be mainly by diffusion but convection through fine pores or voids in the skin may also be important.

In the preferential sorption - capillary flow model developed by Kimura and Sourirajan (1967) the membrane surface is conceived to have pores of a specific size and size distribution and further, that preferential sorption takes place on the membrane surface. If water is preferentially sorbed, solute is repelled from the membrane surface and the solute concentration on the membrane surface will be low thus giving a good rejection. If the solute is preferentially sorbed the solute concentration at the surface will be high and depending on the physico-chemical properties of solute and membrane, rejection may be poor.

4.6

4. Porous support region : The porous substructure of the membrane supports the dense skin and does not affect the overall membrane rejection characteristics. However, the porous layer does add some resistance to the hydraulic permeability of the membrane.
5. Boundary layer low pressure side : There is no concentration polarization in this region and the concentration inside the membrane is essentially the same as in the bulk product side.
6. Bulk region low pressure side : The concentration of solute in this region remains constant at C_p under steady state conditions.

4.2.2 Models from the Thermodynamics of Irreversible Processes

4.2.2.1 General considerations

Since the physical structure of reverse osmosis membranes and the mechanism of solute and solvent transport in these membranes are not fully known and understood, it is useful to apply the thermodynamics of irreversible processes in an attempt to describe the process. In this approach it is assumed that the system can be divided into small subsystems in which local equilibrium exists and for which thermodynamic quantities can be written.

During a spontaneous irreversible process the entropy increases, and free energy is therefore dissipated. The rate of the local dissipation of free energy per unit volume is represented by the dissipation function Φ derived by Katchalsky and Curran (1975) by using the Gibbs equation.

4.7

$$\phi = J_{ent} \cdot \text{grad}(-T) + \sum_{i=1}^n J_i \cdot \text{grad}(-\tilde{\mu}_i) + J_{ch} \cdot \tilde{A}$$

where

- J_{ent} = rate of entropy exchange
- T = absolute temperature
- J_i = molar flux of component i
- $\tilde{\mu}_i$ = electrochemical potential of component i
- J_{ch} = rate of chemical reaction
- \tilde{A} = electrochemical affinity 4.1

Equation 4.1 states that the rate of entropy production can be expressed as the sum of products of fluxes and their conjugated forces.

$$ie \phi = \sum_{i=1}^n J_i X_i \dots\dots\dots 4.2$$

where J_i and X_i are the generalised forced and fluxes respectively.

For a sufficiently slow process a linear dependence exists between all fluxes and all forces - known as the phenomenological equations or linear laws :

$$J_i = \sum_{k=1}^n L_{ik} X_k \quad (i = 1,2,3 \dots\dots n) \dots\dots\dots 4.3$$

This means that in a system with n simultaneous flows J₁-J_n, any flow J_i depends in a direct and linear manner not only on its conjugate forces (denoted by L_{ii}), but also on the non-conjugate forces (denoted by the cross coefficients L_{ij}).

4.2.2.2 Kedem-Katchalsky model

Kedem and Katchalsky (1958) developed the following model based on the thermodynamics of irreversible processes for the transport of non-electrolytes through membranes.

For isothermal non-electrolyte systems in the absence of chemical reaction Equation 4.1 reduces to

$$\dot{\Phi} = \sum_{i=1}^n J_i \text{grad} (-\mu_i) \dots\dots\dots 4.4$$

μ_i = chemical potential of component i.

At steady state J_i remains constant so that Equation 4.4 can be integrated to give :

$$\int_0^{\Delta\chi} \dot{\Phi} dx = \dot{\Phi}_m = \int_0^{\Delta\chi} \sum_{i=1}^n J_i \text{grad} (-\mu_i) dx$$

or $\dot{\Phi}_m = \sum_{i=1}^n J_i \Delta\mu_i \dots\dots\dots 4.5$

where $\dot{\Phi}_m$ is the dissipation function for the whole membrane and $\Delta\chi$ is the membrane thickness.

For a system with only one solute, Equation 4.5 reduces to

$$\dot{\Phi}_m = J_w \Delta\mu_w + J_s \Delta\mu_s \dots\dots\dots 4.6$$

where w and s refer to water and solute respectively. The chemical potential differences are the true thermodynamic driving forces but they are not measurable quantities and they have to be replaced by measurable quantities such as chemical activity and pressure.

4.9

The chemical potential of any component is given by :

$$\mu_i (T,p) = \mu_i^\circ(T,p^\circ) + RT \ln a_i + \bar{V}_i (p-p^\circ) \dots\dots 4.7$$

where $\mu_i (T,p)$ = chemical potential of component i at T and P

$\mu_i^\circ (T,p^\circ)$ = chemical potential of component i at reference pressure p°

a_i = chemical activity of i

\bar{V}_i = partial molar volume of i

R = gas constant

T = absolute temperature

Substituting Equation 4.7 in 4.6 and noting that

$\Delta\mu_i^\circ = 0$, gives

$$\dot{Q}_m = J_w [RT\Delta(\ln a_w) + \bar{V}_w\Delta P] + J_s [RT\Delta(\ln a_s) + \bar{V}_s\Delta P] \dots\dots\dots 4.8$$

where ΔP is the pressure across the membrane

$$\dot{Q}_m = (J_w\bar{V}_w + J_s\bar{V}_s) \Delta P + RT [J_w \Delta(\ln a_w) + J_s\Delta(\ln a_s)] \dots\dots\dots 4.9$$

If the osmotic pressure π is given by

$$\pi = - \frac{RT}{\bar{V}_w} \ln a_w \dots\dots\dots 4.10$$

and according to the van't Hoff Equation :

$$\pi = C_s RT \dots\dots\dots 4.11$$

then, from 4.10 : $RT \Delta(\ln a_w) = -\bar{V}_w \Delta\pi \dots\dots\dots 4.12$

and $\mu_s = RT \Delta(\ln a_s) = RT \ln \frac{(\gamma_s X_s)^\circ}{(\gamma_s X_s)} \dots\dots\dots 4.13$

4.10

where γ_s and x_s are the activity coefficient and mole fraction of the solute respectively. (0 and ∞ denote the high and low pressure sides respectively). For dilute solutions $\gamma_s = 1$, so that Equation 4.13 becomes

$$\frac{1}{RT} \mu_s = \Delta \ln a_s = \ln \frac{C_s^0}{C_s^\infty} = \frac{C_s^0 - C_s^\infty}{(C_s) \ln}$$

$$= \frac{\Delta C_s}{(C_s) \ln} = \frac{1}{RT} \frac{\Delta \pi}{(C_s) \ln}$$

where $(C_s) \ln$ is the log average concentration. Substituting in Equation 4.9; gives

$$\dot{\phi} m = [J_w \bar{V}_w + J_s \bar{V}_s] \Delta P + \left[\frac{J_s}{(C_s) \ln} - J_w \bar{V}_w \right] \Delta \pi \dots\dots 4.14$$

Thus the forces in Equation 4.6 μ_w and μ_s have been transformed to measurable quantities ΔP and $\Delta \pi$.

The conjugate fluxes that satisfy the thermodynamic requirements are

$$[J_w \bar{V}_w + J_s \bar{V}_s] = J_v \text{ and}$$

$$J_D = \left[\frac{J_s}{(C_s) \ln} - J_w \bar{V}_w \right] \text{ which is the velocity of solute}$$

relative to that of solvent . so that

$$\dot{\phi} m = J_v \Delta P + J_D \Delta \pi \dots\dots\dots 4.15$$

The phenomenological Equations 4.2 and 4.3 (linear laws) can now be written as

$$J_v = L_p \Delta P + L_{pD} \Delta \pi \dots\dots\dots 4.16$$

and

4.11

$$J_D = L_{DP} \Delta P + L_D \Delta \pi \dots\dots\dots 4.17$$

Equation 4.16 can be written as

$$J_v = L_p (\Delta P - \sigma \Delta \pi) \dots\dots\dots 4.18$$

where

$$\sigma = \frac{-L_{pD}}{L_p} \dots\dots\dots 4.19$$

σ is the reflection coefficient and
 L_p is the hydraulic coefficient

Equations 4.16 and 4.17 can be added to give

$$J_s = (C_s) \ln [J_v + J_D]$$

If $V_s(C_s) \ln \ll 1$, J_v and J_D can be substituted from Equations 4.16 and 4.17 and if it is assumed that $L_{pD} = L_{DP}$ (Onsager Reciprocal Relations ORR)

$$J_s = (C_s) \ln (1 - \sigma) J_v + \omega \Delta \pi \dots\dots\dots 4.20$$

where $\omega = (C_s) \ln (L_D L_p - L_{pD}^2) / L_p$
 is the solute permeability at zero volume flux.

These two Equations for J_v and J_s (4.18) and (4.20) are known as the Kedem-Katchalsky membrane model and have been used widely in the literature.

The three coefficients in this model L_p , σ and ω are less dependent on concentration than the phenomenological coefficients L_p , L_{pD} , L_{DP} and L_D in Equations 4.16 and 4.17.

4.2.2.3 Spiegler-Kedem Model.

The coefficients L_p , σ and ω are relatively independent of concentration as long as the volume flux and concentration gradients are relatively small. When fluxes and concentration gradients are large J_s will not be adequately represented by the Kedem-Katchalsky equation because the changing concentration profile at different flow rates has to be taken into account.

Thus Spiegler and Kedem (1966) started with the local phenomenological equations

$$J_w = L_{ww} \left(\frac{-d\mu_w}{dx} \right) + L_{ws} \left(\frac{-d\mu_s}{dx} \right)$$

and

$$J_s = L_{sw} \left(\frac{-d\mu_w}{dx} \right) + L_{ss} \left(\frac{-d\mu_s}{dx} \right) \dots\dots\dots 4.21$$

and developed the following expressions for water and solute flux :

$$J_v = p_h \left(\frac{dP}{dx} - \sigma \frac{d\pi}{dx} \right) \dots\dots\dots 4.22$$

where p_h is the local hydraulic permeability given by

$$p_h = -L_{ww} \bar{v}_w^2$$

The solute flux, J_s , is given by

$$J_s = p_s \frac{dC_s}{dx} + (1 - \sigma) C_s J_v \dots\dots\dots 4.23$$

where p_s is the local solute permeability given by

$$p_s = \frac{vRT}{C_s} \left(\frac{L_{ws}^2}{L_{ww}} - L_{ss} \right)$$

4.13

If it is assumed that p_s, σ, J_s and J_v are constant, Equations 4.23 can be integrated for the boundary conditions that

$$\begin{aligned} \text{at } \chi = 0, C_s &= k_s C_f \\ \text{and at } \chi = \Delta\chi, C_s &= k_s C_p \end{aligned}$$

where k_s is the distribution coefficient of solute between membrane and solution. This gives

$$\frac{J_v(1-\sigma)\Delta\chi}{P_s} = \ln \frac{C_p \sigma}{C_p - C_f(1-\sigma)} \dots\dots\dots 4.24$$

Substituting the expression for rejection $R = \frac{1-C_p}{C_f}$ into Equation 4.24 gives :

$$R = \frac{\sigma [1 - e^{-J_v(1-\sigma)\Delta\chi/P_s}]}{1 - \sigma e^{-J_v(1-\sigma)\Delta\chi/P_s}} \dots\dots\dots 4.25$$

Let $P_m = P_s / \Delta\chi$ and $\beta = J_v (1 - \sigma) / P_m$, gives

$$R = \frac{\sigma(e^{\beta} - 1)}{e^{\beta} - \sigma} \dots\dots\dots 4.26$$

The coefficients from this model are less sensitive to large concentration gradients and high fluxes than the Kedem-Katchalsky model. Jagur-Grodzinski and Kedem (1966) found that σ and P_m stayed almost constant for different concentrations of NaCl.

4.2.2.4 Soltanieh-Gill model. The Kedem-Katchalsky and Spiegler-Kedem models are based on the assumptions that Onsager Reciprocal Relations are valid and that transport is by diffusion only. The validity of the Onsager Reciprocal Relations is open to question and specifically at high

flux rates they have been shown not to be valid. Similarly the basic assumption of mechanical equilibrium in thermodynamics of irreversible processes does not take into account any convective effects. In extremely tight perfect reverse osmosis membranes this may not be a problem, but most practical membranes do have micro-pores or voids and convective flow through them contributes to water and solute transport across the membrane.

The total molar flux of any component, N is given by :

$$N_i = J_i + C_i v^* \dots\dots\dots 4.27$$

where J_i = diffusive flux

$C_i v^*$ = convective flux

C_i = local molar concentration of i

v^* = molar-average velocity.

The total water flux, N_w can be given by

$$N_w = J_w + C_w v^* \dots\dots\dots 4.28$$

This means that J_w does not give the total flux when convective flow occurs and N_i should be used rather than J_w in modelling flow across membranes.

Soltanieh and Gill (1981) derived the following transport equations by using $N_i = J_i + C_i v^*$ in the phenomenological Equations 4.20 and 4.21 :

$$N_w = K_1 (\Delta P - \Delta \pi) + K_2 \ln \frac{C_f}{C_p} + \bar{v}_w K_w (C_w) \ln \dots 4.29$$

and

$$N_s = K_3 (\Delta P - \Delta \pi) + K_4 \ln \frac{C_f}{C_p} + \bar{v}_w K_s (C_s) \ln \dots 4.30$$

where $K_1 = \frac{L_{ww} \bar{v}_w}{\Delta x}$; $K_2 = \frac{L_{ws} (\nu RT)}{\Delta x}$

$$K_3 = \frac{L_{sw} \bar{v}_w}{\Delta x}; \quad K_4 = \frac{L_{ss} (\nu RT)}{\Delta x}$$

where $(C_w)_{ln}$ and $(C_s)_{ln}$ are the log mean concentration differences.

The model described by Equations 4.29 and 4.30 is a general one which includes the convection term, does not use the Onsager Reciprocal Relations, and the phenomenological coefficients L_{ij} are determined from data analysis.

4.2.3 Spiegler Frictional Models

Frictional models were introduced by Spiegler (1958) and applied to reverse osmosis membranes by Spiegler and Kedem (1966) and extended by Belfort (1976) to include the effect of bound water in glass membranes.

According to this model the driving forces for transport in steady flow are balanced by frictional forces exerted by the other components. The frictional forces are

$$F_{ij} = f_{ij} (u_i - u_j) \dots\dots\dots 4.31$$

f_{ij} is the friction coefficient between i and j , and u_i and u_j are mean linear velocities of i and j . The total force on water permeating a membrane is then :

$$F_w = f_{sw} (C_s/C_w)(u_w - u_s) + f_{wm} (u_w - u_m) \dots\dots\dots 4.32$$

and on solute

$$F_s = f_{sw} (u_s - u_w) + f_{sm} (u_s - u_m) \dots\dots\dots 4.33$$

where subscript m refers to the membrane

Replacing velocities by fluxes $J = uc$, gives

$$J_w = \frac{F_w(f_{sm} + f_{sw})C_w^2}{d} + \frac{f_{sw}C_wC_s}{d} F_s \dots\dots\dots 4.34$$

and

$$J_s = \frac{f_{sw}C_wC_s}{d} F_w + \frac{C_s(f_{wm}C_w + f_{sw} C_s)}{d} F_s \dots\dots\dots 4.35$$

where $d \equiv f_{sm}f_{wm}C_w + f_{sm} f_{sw} C_s + f_{sw} f_{wm} C_w$.

From these equations Belfort (1976) derived the following equations for the reflection coefficient

$$\sigma = 1 - \left[\frac{C_s/C_s^b}{C_w/C_w^b} \right] \left[\frac{1 + (f_{wm}/f_{sw}) \bar{V}_s/\bar{V}_w}{1 + (f_{sm}/f_{sw})} \right] \dots\dots\dots 4.36$$

$$p_h = (C_w/C_w^b)^2 \frac{(1/f_{wm})(1 + f_{sm}/f_{sw})}{1 + f_{sm}/f_{sw} (1 + f_{ws}/f_{wm})} \dots\dots\dots 4.37$$

and $p_s = 2RT (C_s/C_s^b) \cdot (1/f_{sm}) / (1 + f_{sw}/f_{sm}) \dots\dots\dots 4.38$

where "b" indicates concentrations in the bulk solution.

The first term in each case is the "exclusion" term and the second is the "kinetic" term.

4.2.4 Lonsdale solution-diffusion model

In this model introduced by Lonsdale et al. (1965) it is postulated that the membrane is a homogeneous, non-porous phase. Both water and solute dissolve in the membrane surface layer and are then transported in an uncoupled manner under the driving force of chemical potential by a diffusion mechanism through the membrane. Since the membrane is postulated to be non-porous there is no convective flow. This assumption may be valid for perfect membranes. However, when there are imperfections in the membrane, convective flow may contribute to the total flow of water and solute. To account for this Sherwood et al. (1967) introduced the "solution-diffusion-imperfection" model which allows for convective flow of solute and solvent.

If water flux is by diffusion only through the membrane it may be described by means of a Fick's Law diffusion coefficient :

$$J_w = -D_w \frac{dC_w}{d\chi} \dots\dots\dots 4.39$$

where J_w is the water flux

D_w is the water diffusion coefficient

C_w is the concentration of water dissolved in the membrane

If Henry's Law is obeyed

$$\mu_w = \text{const} + RT \ln C_w \dots\dots\dots 4.40$$

$$\text{and } d\mu_w = RT d \ln C_w = - RT \frac{dC_w}{C_w}$$

where μ_w is the chemical potential of water in the membrane. Equation 4.39 then becomes

$$J_w = \frac{D_w C_w}{RT} \frac{d\mu_w}{dx} \dots\dots\dots 4.41$$

$$\cong \frac{D_w C_w}{RT} \frac{\Delta\mu_w}{\Delta x} \dots\dots\dots 4.42$$

when μ_w is replaced from

$$\mu_i(T,p) = \mu_i^\circ(T,p^\circ) + RT \ln a_i + \bar{V}_i(p-p^\circ) \dots\dots\dots 4.43$$

$$J_w = \frac{D_w C_w}{RT \Delta x} (RT \ln a_w + \bar{V}_w \Delta P) \dots\dots\dots 4.44$$

and from Equation 4.10

$$\pi = \frac{RT}{\bar{V}_w} \ln a_w$$

$$J_w = \frac{D_w C_w \bar{V}_w}{RT \Delta x} (\Delta P - \Delta \pi) \dots\dots\dots 4.45$$

$$\text{or } J_w = A(\Delta P - \Delta \pi) \dots\dots\dots 4.46$$

In arriving at this result it has been assumed that D_w , C_w , \bar{V}_w are independent of pressure, which is reasonable for pressures of interest in reverse osmosis. This equation allows the calculation of the apparent water permeability $D_w C_w$ from water throughput measurements.

If the solute flux is entirely diffusive, the solute concentration gradient constitutes the driving force since the chemical potential difference due to pressure can be regarded as negligible in this case. Solute flux, J_s is then given by

$$J_s = -D_s \frac{dC_s}{d\chi} \dots\dots\dots 4.47$$

$$\approx -D_s \frac{\Delta C_s}{\Delta \chi} \dots\dots\dots 4.48$$

where D_s is the solute diffusion coefficient through the membrane, and C_s is the solute concentration in the membrane.

The solute concentration in the membrane cannot be readily determined, therefore it is related to the external concentration by means of a distribution coefficient, K_s so that $C_s' = K_s C_f$ and $C_s'' = K_s C_p$ (if it is assumed that K_s is independent of concentration), so that

$$J_s = -D_s K_s \frac{(C_p - C_f)}{\Delta \chi} \dots\dots\dots 4.49$$

$$= D_s K_s \frac{(C_f - C_p)}{\Delta \chi}$$

$$= B(C_f - C_p) \dots\dots\dots 4.50$$

This model says that flow of water and solute takes place by uncoupled diffusion of water and solute through the membrane under the gradient of their respective chemical potentials.

The model adequately describes the permeation of water and solute through perfect cellulose acetate membranes (Lonsdale *et al.*, 1965). However in membranes with imperfections and in more open membranes convective flow contributes significantly to solute flux through the membrane.

4.2.4.1 Solution-diffusion-imperfection model. In order to account for imperfect membranes Sherwood *et al.* (1967) extended the solution-diffusion model by adding terms to describe the contribution of convective flows. The total water flux, N_w is then given by

$$N_w = J_w + K' \Delta P C_w \dots\dots\dots 4.51$$

$$= A(\Delta P - \Delta \pi) + K' \Delta P C_w \dots\dots\dots 4.52$$

where C_w is the water concentration in the high pressure side of the membrane. Solute flux, N_s is given by

$$N_s = J_s + K'' \Delta P C_f \dots\dots\dots 4.53$$

$$= B(C_f - C_p) + K'' \Delta P C_f \dots\dots\dots 4.54$$

(where K'' can be viewed as the coupling coefficient)

4.2.4.2 Solubility parameter approach. According to the solution-diffusion mechanism of membrane transport the solubility of solutes in the membrane is an important parameter governing solute transport (in addition to the rate of diffusion of the particular solute in the membrane). The solubility or partition coefficient or distribution coefficient K_s relates the solute concentration inside the membrane to the external solution

$$C_m = K_s C_f.$$

K_s can be determined experimentally by immersing a piece of membrane in a solution of known concentration and measuring the equilibrium concentration of solute in the membrane or the concentration of the solution after equilibrium has been attained.

$$K_s = \frac{\text{mass solute/volume membrane}}{\text{mass solute/volume solution}}$$

It may also be possible to predict K_s values by using an appropriate parameter for the solubility of solutes in the membrane. Solubility parameters introduced by Hildebrand and Scott (1964) may be suitable for this purpose.

Solubility parameter theory predicts that the solvency increases as the solubility parameter δ of the solute approaches that of the solvent.

The process of dissolving a solute in a solvent is governed by the free energy equation $\Delta G = \Delta H - T\Delta S$.

where ΔH is heat of mixing

and ΔS is entropy of mixing

If ΔG is negative the process will occur spontaneously.

Since dissolution is always connected with a relatively large increase in entropy, the magnitude of the heat term ΔH is the deciding factor in determining the sign of the free energy change. Hildebrand and Scott (1964) proposed that

$$\Delta H_m = V_m \left[\frac{(\Delta E_1)^{\frac{1}{2}}}{(V_1)^{\frac{1}{2}}} - \frac{(\Delta E_2)^{\frac{1}{2}}}{(V_2)^{\frac{1}{2}}} \right]^2 \cdot \phi_1 \phi_2 \quad \dots\dots\dots 4.55$$

where ΔH_m is the overall heat of mixing

V_m is the total volume of mixture.

ΔE is the energy of vapourization

ϕ is the volume fraction of component 1 or 2 in the mixture.

Rearranging Equation 4.55 gives

$$\frac{\Delta H_m}{V_m \phi_1 \phi_2} = \left[\frac{(\Delta E_1)^{\frac{1}{2}}}{(V_1)^{\frac{1}{2}}} - \frac{(\Delta E_2)^{\frac{1}{2}}}{(V_2)^{\frac{1}{2}}} \right]^2 \quad \dots\dots\dots 4.56$$

and by defining the solubility parameter, δ as

$$\delta = \frac{(\Delta E)^{\frac{1}{2}}}{(V)^{\frac{1}{2}}} \quad \dots\dots\dots 4.57$$

gives
$$\frac{\Delta H_m}{V_m \phi_1 \phi_2} = (\delta_1 - \delta_2)^2 \dots\dots\dots 4.58$$

This states that the heat of mixing per unit volume equals the square of the difference between the square roots of the cohesive energy densities of the components.

This means that if the heat of mixing of two components is not to be so large as to prevent mixing, $(\delta_1 - \delta_2)^2$ has to be relatively small. In other words if the δ values of two substances are nearly equal the substances will be miscible. The solubility parameter of a solvent is readily calculable but the solubility parameter of a polymer cannot be determined directly and is therefore defined as the solubility parameter of a solvent in which the polymer will mix in all proportions without heat change, without volume change and without reaction or association.

Hansen et al. (1971) extended the solubility parameter theory by introducing the following partial solubility relations so that

$$\delta T^2 = \delta d^2 + \delta p^2 + \delta h^2 \dots\dots\dots 4.59$$

where

δT = total solubility parameter

δd = partial solubility parameter due to dispersion interactions

δp = partial solubility parameter due to polar interactions

δh = partial solubility parameter due to hydrogen bonding interactions

The solubility of solutes in a membrane may be correlated with either the total solubility parameter or one or more of the partial solubility parameters depending on the characteristics of the membrane. The rate of diffusion which is the other parameter governing solute rejection or transport is a function mainly of the hydrodynamic volume and shape of the solute molecule. By incorporating these two parameters in the solution-diffusion model it can be used as a predictive model for solute rejection.

- 4.2.4.3 Solvophobic theory. In sorption reactions, solvent properties play an important role in addition to the properties of the adsorbent and sorbate (or solute). In reverse osmosis, the rejection of solute (or transport of solute through the membrane) is governed by an equilibrium effect (sorption or dissolution) and a kinetic or transport effect (diffusion). It is therefore also important in an analysis of reverse osmosis processes to consider the effect of the solvent (water) on the equilibrium sorption process of solute by the membrane.

The solvophobic theory developed by Sinanoglu (1968) presents a comprehensive fundamental basis for describing the interactions between solute and solvent in association reactions. In this theory the effect of the solvent on the association reaction is obtained by subtracting the standard free energy change for the reaction in the gas phase from the standard free energy change in solution.

In order to conceptualize the solvent effect it has been proposed that the dissolution process of solute in solvent takes place in two steps as illustrated in Figure 4.2. First, a hole or cavity needs to be prepared in the solvent to accommodate the solute molecule; second, after the solute is placed into the cavity, it interacts with the solvent.

Conceptually, this hypothetical process is the reverse of the solubility parameter approach in which bond disruption analogous to vaporization is proposed.

The energy associated with the formation of the cavity, ΔG_{cav} , is proportional to the surface area of the solute molecule and the corrected macroscopic surface tension of the solvent to take into account the curved rather than flat surface of the solute.

Transferring a solute molecule from the gas phase into the solvent is accompanied by an entropy reduction. This free volume reduction has been termed the cratic term and is calculated directly from $RT \ln (RT/PV)$. The energies related to cavity formation and free volume change both have the same sign.

After the solute is placed into the prepared cavity, it will interact with the solvent. This energy of interaction, ΔG_{int} , comprises :

- . van der Waals interactions due to dispersion forces, ΔG_{vdw} , which are roughly proportional to the molecular surface area

- electrostatic interactions, ΔG_{es} , which are partly dependent on the dipole moment of the solute and the dielectric constant of the solvent. These energies are usually opposite in sign to the energies associated with cavity formation and of the free volume change.

For an association process individual free energies as shown in Figure 4.2 are evaluated for each species, k , and summed to obtain a nett free energy change associated with the solvent effect. Thus :

$$\Delta G_j = \Delta G_j (\text{prod}) - [\Delta G_j (\text{reac.A}) + \Delta G_j (\text{reac.B})] \dots\dots\dots 4.60$$

for an association process



where j is the type of interaction described above, such as the cavity, van der Waals, and electrostatic terms. The nett solvent effect is given by :

$$\Delta G_{\text{solvent}}^{\text{nett}} = \Delta G_{\text{cav}}^{\text{nett}} + \Delta G_{\text{vdw}}^{\text{nett}} + \Delta G_{\text{es}}^{\text{nett}} - RT \ln (RT/PV) \dots\dots\dots 4.62$$

Each of these terms can be calculated with a knowledge of the physico-chemical properties of each species using detailed expressions from the literature.

Figure 4.3 originally published by Horvath and Melander (1978) was adapted by Belfort (1980) for the adsorption process. It illustrates the surface area reduction and the interactions resulting from the solvent effect.

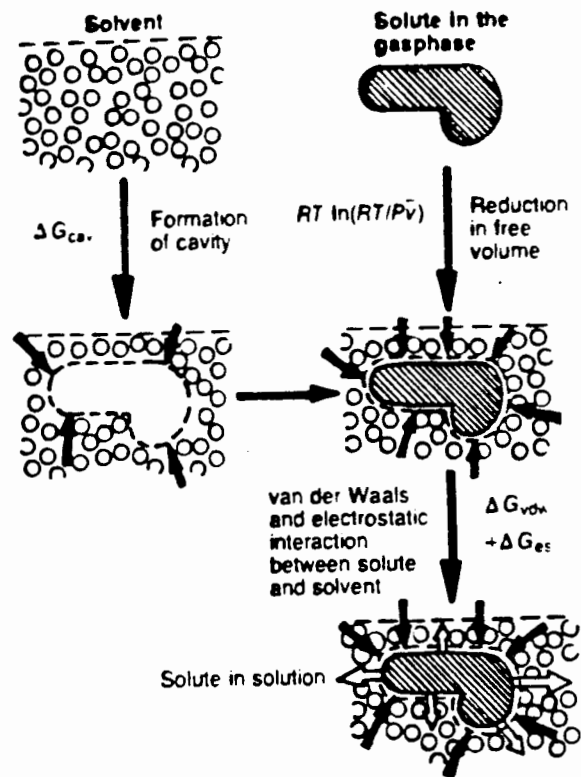


FIGURE 4.2 ILLUSTRATION OF THE SOLVENT EFFECT ON AN ASSOCIATION REACTION (Belfort, 1980)

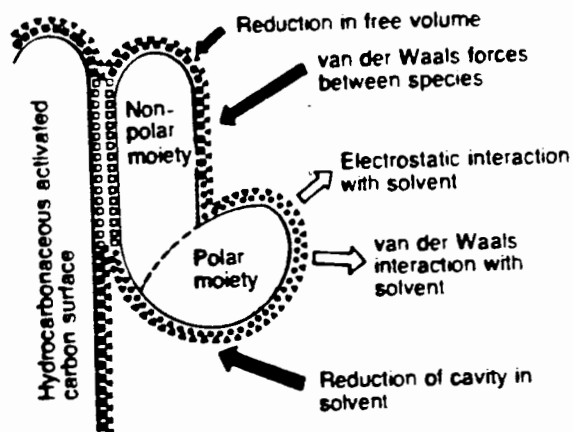


FIGURE 4.3 ILLUSTRATION OF SURFACE AREA REDUCTION AND INTERACTION OF FORCES IN THE ADSORPTION OF AN AMPHIHILIC SOLUTE BY ACTIVATED CARBON (Belfort, 1980)

4.26

The following expressions define the unitary free energy change for the interaction processes

Cavity formation
$$\Delta G_{cav}^{nett} = K_i e^{A_i \sum_{j=1}^i (1-w) N_j} \dots\dots\dots 4.63$$

Solvent-solute interaction
van der Waals
$$\Delta G_{vdw}^{nett} = -f (Q'Q'') B_i \Delta_i D_i D \dots\dots\dots 4.64$$

Electrostatic
$$\Delta G_{es}^{nett} = - \frac{N_i \mu_i^2}{2 V_i} DP \dots\dots\dots 4.65$$

The overall standard free energy change for the association adsorption reaction in solution is calculated from

$$\Delta G_{solvent}^{assoc} = \Delta G_{solvent}^{nett} + \Delta G_{gas}^{assoc} \dots\dots\dots 4.66$$

$$\Delta G_{solvent}^{assoc} = \Delta G_{gas}^{assoc} + \left[\Delta G_{cav} + \Delta G_{vdw} + \Delta G_{ES} \right] \Delta G_{Prod-A-B}^{nett}$$

$$-RT \ln \frac{RT}{P^0 V} \dots\dots\dots 4.67$$

Belfort (1981) in his adaptation of the solvophobic theory to adsorption of dissolved organics by active carbon from dilute aqueous solutions related $\Delta G_{solvent}$ through the equilibrium constant to the adsorption capacity P_i for different solutes.

$$\Delta G_{\text{Solvent}}^{\text{assoc}} = RT \ln \bar{P}_i + \theta \dots\dots\dots 4.68$$

where $\theta = RT \ln [C]$ which is a constant for dilute solutions and a given carbon

$$\bar{P}_i = [C] K_{\text{soln}} = \frac{Y_i}{X_i} \text{ where } Y_i \text{ is amount of solute}$$

adsorbed per unit mass of carbon at equilibrium concentration X_i .

In principle the comprehensive theory can be correlated with adsorption (Belfort et al., 1984). However, this is a very complicated procedure and it has been found that the theory can be simplified since the inverse volume forces dominate for small molecules and, as the relative size of solute molecules increase, surface forces predominate (Halicioglu and Sinanoglu 1969). Belfort et al. (1984) concluded that for aqueous adsorption dominated by hydrophobic interactions only the total solute molecular surface area is required to predict adsorption capacity on activated carbon.

The solvophobic theory should conceptually also be applicable to reverse osmosis separation of dissolved organics from dilute aqueous solutions since according to the solution-diffusion and related mechanisms of separation solute transport across the membrane is the result of an association reaction between solute and membrane (dissolution or sorption) followed by a transport process (diffusion). The possible application of the solvophobic theory to membrane transport is discussed in detail in Section 4.3

4.2.5 Sourirajan preferential sorption-capillary flow model

This model introduced by Kimura and Sourirajan (1967) postulates that the surface layer of the membrane is microporous and heterogeneous and that solute separation is governed by surface phenomena (preferential sorption) and fluid transport

under pressure through capillaries. The important parameters determining water and solute transport are therefore (i) the chemical nature of the membrane material, the solute and the solvent, and (ii) the pore size and pore size distribution on the surface of the membrane.

This means that if a given membrane in contact with a solution has a strong preferential sorption for one component of the solution a steep concentration gradient will develop at the surface with essentially a pure layer of this component in contact with the membrane. If water is preferentially sorbed by the membrane the layer of pure water is then forced through the membrane capillaries under pressure. Polymeric membranes with low dielectric constant, such as cellulose acetate, repel ions in the close vicinity of the surface thus preferentially sorbing water at the surface, and with an appropriate pore structure desalinated water is transported under pressure through the membrane. The process of preferential sorption and capillary flow under pressure is shown schematically in Figure 4.4 (Sourirajan 1970).

This theory has been developed extensively for reverse osmosis separation of dissolved organics from dilute aqueous solutions; initially for cellulose acetate membranes (Matsuura and Sourirajan 1971) and later also for aromatic polyamide membranes (Dickson *et al.*, 1975).

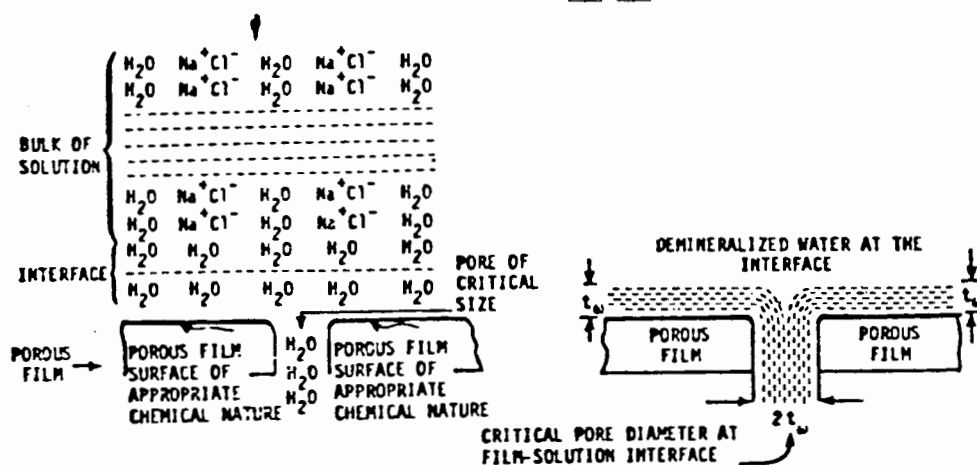


FIGURE 4.4 SCHEMATIC ILLUSTRATION OF PREFERENTIAL SORPTION-CAPILLARY FLOW MODEL

The theory divides solute-solvent-membrane interactions into three basic components viz polar, non-polar and steric interactions. They developed a set of parameters describing the solute characteristics and a set of related parameters describing the solute-membrane interactions. Together these two sets of parameters are then used to determine solute transport parameters which are then used in the transport equations.

(i) Polar free energy :

The polar nature of the solute may be represented by any of the following :

- the hydrogen bonding ability as given by ΔV_S (acidity) (Matsuura and Sourirajan 1971).
- the dissociation constant; Long range coulombic forces cause the repulsion of ions at the membrane interface. The dissociation constant is the ultimate form of ΔV_S when hydrogen and other bonds are broken (Matsuura and Sourirajan 1971).
- Taft (σ^* , $\Sigma\sigma^*$) and Hammett (σ , $\Sigma\sigma$) constants for the substituent group in the molecule. Tabulated values are used which represent the electron withdrawing ability of the substituent group with respect to a reference substituent. This determines the nature of the electron cloud at the functional group. (Matsuura and Sourirajan, 1971).
- The interfacial polar free energy parameter for unionised solutes or dissociated ions

$$-\frac{\Delta\Delta G}{RT} = \frac{1}{RT} (\Delta G_I - \Delta G_B) \dots\dots\dots 4.69$$

representing the energy required to bring an ion or non-ionised solute from the bulk solution to the membrane solution interface. ΔG_I , ΔG_B represent the free energy change at the interface and in the bulk solution respectively.

The quantity $\frac{-\Delta\Delta G}{RT}$ which is an interfacial property is a function of the chemical nature of the solute, the solvent and the membrane material and is independent of the porous structure of the membrane (Matsuura *et al.*, 1976).

(ii) Non polar parameter $W^* \Sigma S^*$

This parameter represents the hydrophobic interaction at the membrane-solution interface. A direct measure of the non-polar character of a hydrocarbon molecule is given either by its molar solubility in water or by its molar attraction constant as given by Small's number. A decrease in solubility or increase in Small's number indicates an increase in hydrophobicity. Sourirajan derived a "modified Small's number" ΣS^* which can be obtained from its chemical structure using the additive property of S^* for different structural groups. ΣS^* represents the property of the solute in the bulk phase. The coefficient W^* is a function of the chemical nature of the interface and has to be obtained experimentally.

Hydrophobic interactions are determined by the number of carbon atoms and degree of branching in the molecular structure of the solute and the chemical nature of the membrane surface. An increase in the value of W^* denotes greater non-polar attraction of the solute towards the membrane. For example, the solubility of alcohol in water increases with an increase in the degree of branching. An increase in solubility means greater solute-water attraction which tends to decrease the solute-polymer attraction and this is expressed by a decrease in the value of W^* . On the other hand, an increase in the carbon number tends to increase the value of W^* . When these opposing values cancel each other W^* becomes zero. (W^* is arbitrarily set = 0 for solute molecules containing no more than three straight chain carbon atoms not associated with a polar functional group).

(iii) Steric parameters $\epsilon^* \Sigma E_S$

Steric hindrance arises from repulsions between non-bonded atoms and also from interference of groups or atoms with each other's motions. Consequently steric hindrance is always a repulsive force at the interface. It parallels the effective size of the molecules concerned and is a function not only of the chemical nature of solute, solvent and membrane but also of the porous structure of the membrane surface.

The value of ΣE_S for the substituent group in the solute molecule depends only on the chemical nature of the group and represents the property in the bulk solution phase and may be obtained from tables given by Taft (1956).

The steric coefficient δ^* associated with \bar{E}_S depends on the chemical nature of the functional group in the solute molecule, as well as the chemical nature and porous structure of the membrane surface. The quantity δ^* therefore has to be determined experimentally for different groups of compounds e.g. alcohols and for the particular membrane under consideration e.g. cellulose acetate with a particular porous structure. Sourirajan and Matsuura (1978) have compiled graphs and tables giving the value of δ^* for different groups of compounds as a function of NaCl permeability for cellulose acetate and polyamide hydrazide membranes.

4.2.5.1 Transport equations

These equations are based on the following :

- (i) pure water permeation rate (PWP) is directly proportional to the operating pressure (ΔP).
- (ii) solvent transport (water) N_w through the membrane is proportional to the effective pressure ($\Delta P - \Delta \pi$).
- (iii) Solute transport (N_s) through the membrane is due to pore diffusion through the membrane capillaries and proportional to the concentration difference across the membrane (not bulk concentration difference but actual concentration difference between high and low pressure sides of the membrane).

4.33

(iv) the mass transfer coefficient K_m on the high pressure side is given by the "film" theory on mass transport and is obtained from

$$K_m = K_{NaCl} \left[\frac{(D_{sw})_{solute}}{(D_{sw})_{NaCl}} \right]^{2/3} \dots 4.70$$

where $(D_{sw})_{solute}$ is the diffusivity of the solute in the feed solution and $(D_{sw})_{NaCl}$ the diffusivity of NaCl in the reference feed solution.

$$A = \frac{PWP}{M_w} \times S \times 3600 \times \Delta P \dots\dots\dots 4.71$$

$$N_w = A \left[\Delta P - \pi(X_{s2}) + \pi(X_{s3}) \right] \dots\dots\dots 4.72$$

$$N_s = \frac{(D_{sm})}{(K \epsilon)} \frac{(1-X_{s3})}{(X_{s3})} (C_2 X_{s2} - C_3 X_{s3}) \dots\dots 4.73$$

$$= K_m C_1 (1-X_{s3}) \ln \left[\frac{X_{s2} - X_{s3}}{X_{s1} - X_{s3}} \right] \dots\dots 4.74$$

- A = pure water permeability constant
- M_w = molecular mass of water
- S = effective membrane area
- X_s = mol fraction of solute
- C = molar density of solution
- Subscript 1 = bulk feed solution
- 2 = concentrated boundary solution
- 3 = permeate
- K_m = mass transfer coefficient at high pressure side.

It is emphasized (Sourirajan and Matsuura, 1978) that neither any one of this set of equations nor any part is adequate representation of reverse osmosis transport which is governed simultaneously by the entire set of equations. In addition these equations are valid only for those cases where water is preferentially sorbed at the membrane surface (i.e. they do not hold for the separation of phenol and higher alcohols). These equations are similar to those of the solution-diffusion model except that the concentration in the membrane surface is related to the bulk concentration by the film theory and not a partition coefficient.

The solute transport parameter $\frac{D_{sm}}{K_m \delta}$ is treated as a single quantity and is independent of feed concentration for non-ionised solutes and cellulose acetate and polyamide hydrazide membranes. The theory tries to predict this quantity from the physico-chemical quantities discussed above (i-iii).

The following relationship has been derived to predict K_m (Matsuura et al., 1976) :

$$\ln \frac{D_{sm}}{K_{\delta}} = \ln C^*_{NaCl} + \frac{(-\Delta\Delta G)}{RT} + \delta^* E_s + W^* \Sigma S^* \dots\dots\dots 4.75$$

where $\ln C^*_{NaCl}$ is a constant representing the porous structure of the membrane surface expressed in terms of $\frac{(D_{sm})}{(K_m \delta)_{NaCl}}$

For dilute solutions where the osmotic pressures involved are very small (Matsuura and Sourirajan 1976)

$$\frac{D_{sm}}{K_m \delta} = VS \left(\frac{1-f}{f} \right) \left[\frac{\exp(V_s)}{(K_m)} \right]^{-1} \dots\dots\dots 4.76$$

and

$$f = \left[1 + \frac{D_{sm}/K_m \delta \exp(V_s)}{VS (K_m)} \right]^{-1} \dots\dots\dots 4.77$$

where V_s = permeation velocity
 f = fractional solute separation

4.2.6 Finely-porous model

This is a combined viscous flow and frictional model developed by Merten (1966) using a balance of applied and frictional forces.

The model applies to porous membranes where coupling is through the viscous flow. Separation is achieved only if the solute concentration in the pores differ from that in the bulk solution. Total volume flux is described by Poiseuille's law :

$$\epsilon u = \frac{-\epsilon r_p^2}{8\mu} \frac{dP}{d\chi} \dots\dots\dots 4.78$$

$$= + \frac{\epsilon r_p^2 p}{8\mu} \frac{\Delta P}{\tau \Delta \chi} \dots\dots\dots 4.79$$

where u is the local centre of mass velocity
 ϵ is the fractional open area
 μ is the viscosity of the pore fluid
 r_p is an equivalent pore size
 $\Delta \chi$ is the membrane skin thickness
 τ is the tortuosity

The total solute flux is the sum of viscous flow and diffusional flow with respect to centre of mass $N_S = C_S u + J_S$, and the rejection may be calculated from

$$1-R = \frac{C_p}{C_f} = \frac{K's \exp(u_T \delta / Ds)}{K''s - \epsilon + \epsilon \exp(u_T \delta / Ds)} \dots\dots\dots 4.80$$

4.2.7 General Discussion of Models

The models discussed in this section differ in many respects and some models are applicable only to certain membranes under certain conditions. The models based on the thermodynamics of irreversible processes should be applicable to a wide spectrum of membranes since the model does not incorporate a transport mechanism. The membrane is treated as a black box in which relatively slow processes are taking place near equilibrium. In contrast, the solution-diffusion model applies only to membranes with a homogeneous non-porous skin layer, while the preferential sorption-capillary flow model assumes that the surface layer is micro-porous and heterogeneous and that the size and number of pores in the membrane skin are important characteristics in determining the membrane performance. Some of these models are relatively simple, for example the solution-diffusion model employs only two coefficients (A in Equation 4.46 and B in Equation 4.50), the Kedem-Katchalsky model has three coefficients L_p , ω and σ (Equations 4.18 and 4.20) while the preferential sorption-capillary flow model employs a number of parameters (Section 4.2.5).

- (i) Irreversible thermodynamics models : These models do not incorporate a transport mechanism and do not include any convection effects. The driving force for the transport of solute and solvent is the potential gradient and in this respect they are, therefore, similar to the solution-diffusion models. Since the membranes used in this study have very high rejection characteristics for sodium chloride it can be assumed that the contribution of convective transport to the total transport will be very small and can, therefore, be disregarded.

Solvent transport is linearly dependent on the pressure driving force and can therefore be represented by linear models such as the Kedem-Katchalsky model

$$J_v = L_p (\Delta P - \sigma \Delta \pi)$$

as is shown in Sections 4.4 and 4.5. The solute flux, on the other hand, is not linearly dependent on driving forces since the coefficients in the simple models such as the Kedem-Katchalsky model vary with concentration.

The relation between solvent and solute flux (or volume flux and rejection) is important since rejection reaches an asymptotic maximum as the volume flux increases. Pusch (1977) derived the following relationship from the Kedem-Katchalsky model by starting with

$$J_v = L_p (\Delta P - \sigma \Delta \pi) \dots\dots\dots 4.18$$

$$\text{and } J_s = (C_s)_{ln} (1 - \sigma) J_v + \omega \Delta \pi \dots\dots\dots 4.20$$

Introducing

$$R = 1 - C_p/C_f = 1 - J_s/C_f J_v \text{ and}$$

$$\text{Substituting } \omega = (C_s)_{ln} (L_D L_p - L_{pD}^2)$$

he obtained

$$R = 1 - (1 - \sigma)(C_s)_{ln}/C_f - (L_D/L_p - \sigma^2) (C_s)_{ln}/C_f \cdot L_p / J_v \dots\dots\dots 4.81$$

$$\text{as } J_v \rightarrow \infty, R_x = 1 - (1 - \sigma)(C_s^\infty)_{ln}/C_f \dots\dots\dots 4.82$$

However, $(C_s^\infty)_{ln} \cong C_f$ and

$$\text{therefore } R_x = \sigma \dots\dots\dots 4.83$$

By replacing $\Delta \pi$ by $\pi_R R$

$$1/R = 1/R_x + (L_D/L_p - R_x^2) L_p \pi_R / R_x \cdot 1/J_v \dots\dots\dots 4.84$$

A plot of $1/R$ vs $1/J_v$ should give a straight line with an intercept of $1/R_x$ and a slope of $(L_D/L_P - R_x^2)L_P \pi r/R_x$. This model (4.84) will be checked for NaCl solutions (Section 4.4) and for organic solutions (Section 4.5).

- (ii) Solution-diffusion models. These models are based on the assumption of solute and solvent dissolution into the membrane and diffusive transport across the membrane. Solvent transport can be represented by Equation 4.46 : $J_v = A(\Delta P - \Delta \pi)$ while solute transport is represented by Equations 4.49 and 4.50 :

$$J_s = D_s K_s \frac{(C_f - C_p)}{\Delta x}$$

This model can be used in a simple predictive manner if values for D_s and K_s for a particular solute and a membrane can be determined from solute and membrane characteristics. Studies on these aspects are reported in Section 4.5 for phenol and different membranes.

This model may be modified or adapted by substituting K_s with another parameter. An attempt was made by Spencer and Gaddis (1979) to use the solubility parameter δ for this purpose. They derived a solubility parameter δ_m for the membrane and correlated the difference between δ_m and δ solute with the rejection of different solutes. This correlation was not very successful mainly because the correlation did not take a transport parameter such as solute diffusivity into consideration.

In Section 4.3 an attempt is made to replace K_s by a parameter from the solvophobic interaction theory together with a factor to account for transport across the membrane.

(iii) The Preferential Sorption-Capillary Flow Model : This model has been developed extensively by Sourirajan and co-workers and many papers have been published on the use of this model to predict solute rejection by different membranes (Matsuura and Sourirajan, 1971; 1978 and Matsuura et al., 1974; 1976; 1977). Reasonably good correlations have been obtained between the theory and experimental observations. There are, however, a number of points of criticism against this model i.e.

- . This is not a simple model. It is quite a complicated procedure to predict the rejection of a particular solute by a membrane. A number of adjustable parameters and coefficients have to be obtained for different groups of solutes, for different membrane materials and for different pore sizes and size distributions.
- . The basic transport equations assume that solute transport is entirely due to diffusion. This assumption is reasonable for very dense membranes but in more open membranes the contribution of convective flow must be taken into account. This is true especially for membranes with relatively low $\ln C^*NaCl$ and for organics such as the lower alcohols (Matsuura et al., 1977), ethers, ketones, aldehydes and alcohols (Dickson et al., 1975) which are rejected poorly and for which the repulsive force at the membrane interface is not very strong. Convective solute transport is a function of operating pressure and solute concentration, and this fact is not considered in the theory or model.
- . The model is not applicable where solute is preferentially sorbed at the membrane interface. This excludes a large number of organics which are relevant in water reclamation applications such as phenols, higher alcohols, benzenes etc.

4.3 ADAPTATION OF THE SOLVOPHOBIC THEORY TO REVERSE OSMOSIS MEMBRANE TRANSPORT

Theory. In the discussion which follows an attempt is made to describe differences in alcohol separation by reverse osmosis membranes from the fundamental multidimensional approach of the solvophobic theory introduced in Section 4.2.4.3.

Solute separation is a function of the forces of attraction/repulsion between solute and membrane material, and the rate of diffusion of solute across the membrane relative to the diffusion rate of water. This presentation should hold irrespective of the transport model used or mechanism proposed. These two effects i.e. equilibrium effect of sorption/dissolution and kinetic effect of permeation/diffusion are determined by solute-solute, solute-solvent and solute-membrane interactions. In this discussion solute-solute interactions will be ignored since only single solute solutions are considered.

Sorption or dissolution is determined by the interactions described in Section 4.2.4.3 for sorption of solutes on activated carbon. This description by Belfort *et al.* (1984) for selective adsorption of organics onto activated carbon may be adapted for membrane sorption as follows :

Conceptually, solute sorption by the membrane polymer may be represented by the following reversible association reaction



where S_i is the sorbing solute, M is the membrane polymer and S_iM is the sorbed solute-polymer complex. The equilibrium constant for this reaction, K_{solvent} is related to the overall free energy change as follows

$$\Delta G_{\text{solvent}}^{\text{assoc}} = -RT \ln K_{\text{solvent}} \quad \dots\dots\dots 4.86$$

4.41

The solvophobic theory takes into account the effect of the solvent on the above association reaction by considering two hypothetical steps, creation of a cavity in the solvent and interaction of the solute with the surrounding solvent.

The effect of the solvent may be calculated from the difference of the free energy changes of the solvent and gas-phase reactions

$$\Delta G_{\text{solvent effect}}^{\text{nett}} = \Delta G_{\text{solvent}}^{\text{assoc}} - \Delta G_{\text{gas}}^{\text{assoc}} \dots\dots 4.87$$

In addition, this solvent effect is due to the interaction of each species with the solvent. Therefore,

$$\Delta G_{\text{solvent effect}}^{\text{nett}} = \sum_j [\Delta G_{j, \text{SiM}} - \Delta G_{j, \text{Si}} - \Delta G_{j, \text{M}}]_{\text{nett}} \dots\dots\dots 4.88$$

where subscript j represents all possible interactions. Combining Equations 4.87 and 4.88 gives

$$\Delta G_{\text{solvent}}^{\text{assoc}} = \Delta G_{\text{gas}}^{\text{assoc}} + \left[\Delta G_{\text{cav}} + \Delta G_{\text{vdw}} + \Delta G_{\text{es}} \right]_{\text{SiM-(Si-M)}}^{\text{nett}} - RT \ln RT/PoV \dots\dots\dots 4.89$$

The free energy change for cavity formation is calculated (Sinanoglu, 1968) as

$$\Delta G_{\text{cav}, i} = \gamma A K e^{(1-W)^N} \dots\dots\dots 4.90$$

where W is given by

$$W = \left[1 - \frac{k_i e}{K_i S} \right] \left[\frac{d \ln \gamma}{d \ln T} + \frac{2}{3} a_i T \right] \dots\dots\dots 4.91$$

The van der Waals' interaction is represented by a Kihara potential :

$$\Delta G_{vdw,i} \cong -\Delta_i D_i D(0,606 Q) \dots\dots\dots 4.92$$

where

$$\Delta_i = \frac{1,35 I_i I}{I_i + I}; \quad D_i = \frac{n D_i^{2-1}}{n D_i^{2-2}} \dots\dots\dots 4.93, 4.94$$

for solute i ; nonsubscript variables refer to the solvent. Also

$$Q = V_i \left[\frac{\bar{\sigma}^6}{(R - T)^9} \left(\frac{t^2}{11} + \frac{t}{5} + \frac{1}{9} \right) - \frac{1}{(R - 1)^3} \left(\frac{t^2}{5} + \frac{t}{2} + \frac{1}{3} \right) \right] \dots\dots\dots 4.95$$

where

$$t = \left(\frac{\bar{I}}{R - T} \right); \quad R_i = 1,74 \left(\frac{3 V_i}{4 \pi} \right)^{1/3} \dots\dots\dots 4.96, 4.97$$

$$l_i = R_i \left(\frac{0,24 + 7 \omega_i}{3,24 + 7 \omega_i} \right); \quad \sigma_i = \left(\frac{3 V_i}{4 \pi} \right)^{1/3} \left(\frac{4,64}{3,24 + 7 \omega_i} \right) \dots\dots\dots 4.98, 4.99$$

R_i , l_i and σ_i are the molecular diameter, Kihara parameter, and London parameter respectively. The overbar variables indicate the mean value of the solute and solvent parameters.

The electrostatic interactions may be estimated from

$$\Delta G_{es,i} = \frac{-N}{2} \frac{\mu_i^2 DP}{V_i} \dots\dots\dots 4.100$$

$$D = \frac{2(\epsilon - 1)}{2\epsilon + 1}; \quad P = \left[4\pi\epsilon \left(1 - \frac{D\alpha_i}{V_i} \right) \right]^{-1} \dots\dots\dots 4.101, 4.102$$

Substituting Equations 4.100 - 4.102 into Equation 4.89

$$\begin{aligned} \Delta G_{solvent}^{assoc} &= \Delta G_{gas}^{assoc} + \left[\Delta G_{vdw,SiM} - \frac{N}{2} \frac{\mu^2_{SiM} DP}{V_{SiM}} \right. \\ &\quad \left. + NK_{SiM}^e A_{SiM} \gamma_{w,SiM} (1 - W_{SiM}) \right] \\ &\quad - \left[\Delta G_{vdw,Si} - \frac{N}{2} \frac{\mu^2_{Si} DP}{V_{Si}} + NK_{Si}^e \gamma_{w,Si} A_{Si} (1 - W_{Si}) \right] \\ &\quad - \left[\Delta G_{vdw,M} - \frac{N}{2} \frac{\mu^2_M DP}{V_M} + NK_M^e A_M \gamma_{w,M} (1 - W_M) \right] \\ &\quad - RT \ln (RT/PoV) \dots\dots\dots 4.103 \end{aligned}$$

This equation includes all the solvent-solute interactions. However, further simplification is needed to make the problem tractable. Since Van der Waals' physical interactions (hydrophobic or non-polar interactions) play a dominant role in the sorption of non-polar solutes (or non-polar moieties) by the relatively non-polar polyamide membrane only these interactions will be considered.

To simplify the algebra, the molecular volume of the polymer-solute complex SiM may be expressed as a multiple of the solute molecular volume,

$$V_{SiM} = \lambda V_{Si} \dots\dots\dots 4.104$$

where λ is the proportionality constant. It was shown that the actual value of λ has only a very small effect on $\Delta G_{\text{solvent}}$ (Belfort, 1981).

Because of the association sorption reaction of solute S onto sorbent M the total surface area in contact with the free solvent is reduced by,

$$\Delta A = A_{Si} + A_M - A_{SiM} \quad \dots\dots\dots 4.105$$

Substituting the above assumptions into Equation 4.103 gives

$$\begin{aligned} \Delta G_{\text{solvent}}^{\text{assoc}} &= \Delta G_{\text{gas}}^{\text{assoc}} - \Delta G_{\text{vdw},Si} + \frac{N(\lambda - 1) \mu_{Si}^2}{2\lambda V_{Si}} \text{ DP} \\ &- N\gamma\Delta A - N\gamma V^{2/3} (K^e - 1) \frac{A_{Si}}{V_{Si}^{2/3}} - RT \ln \frac{RT}{P_0V} \end{aligned} \quad \dots\dots\dots 4.106$$

The free energy change of the association reaction may be related to its equilibrium constant by

$$\Delta G_{\text{solvent}}^{\text{assoc}} = -RT \ln K_{\text{solvent}} \quad \dots\dots\dots 4.107$$

where

$$K_{\text{solvent}} = \frac{x_{SiM}}{(x_{Si} x_M)} \quad \dots\dots\dots 4.108$$

For dilute solutions

Equation 4.96 may be rearranged to give,

$$\Delta G_{\text{solvent}}^{\text{assoc}} = -RT \ln \frac{x_{SiM}}{x_{Si}} + RT \ln x_M \quad \dots\dots\dots 4.109$$

and therefore,

$$\ln \frac{x_{SiM}}{x_{Si}} = -\frac{\Delta G_{\text{solvent}}^{\text{assoc}}}{RT} + \ln x_M \quad \dots\dots\dots 4.110$$

or

$$\begin{aligned} \ln \frac{x_{SiM}}{x_{Si}} = & - \frac{\Delta G_{gas}^{assoc}}{RT} + \ln x_m + \frac{\Delta G_{vdw, si}}{RT} \\ & - \frac{N(\lambda - 1)}{2\lambda} \frac{\mu_{Si}^2}{V_{Si}} \frac{DP}{RT} + \frac{N\gamma\Delta A}{RT} \\ & + \frac{N\lambda}{RT} V^{2/3} (K^e - 1) \frac{A_{Si}}{V_{Si}} + \ln \frac{RT}{P_0V} \dots\dots\dots 4.111 \end{aligned}$$

The first two terms on the right hand side can be considered constant, and therefore

$$\ln \frac{x_{SiM}}{x_{Si}} \propto V_{dw} + E_s + CAV + CRAT = \Delta G_{net}/RT \dots\dots\dots 4.112$$

where $\ln \frac{x_{SiM}}{x_{Si}}$ can be considered a "partitioning" term.

The validity of the theory may be tested by correlating the adsorption or partitioning term, $\ln \frac{x_{SiM}}{x_{Si}}$, with $\Delta G_{net}/RT$, which represents the solvophobic interactions. The theory may, however, be greatly simplified by noting that the total cavity surface area (TSA) is linearly related to the reduced microsurface area ΔA due to the association reaction and should therefore describe the free energy for cavity formation ΔG_{cav} . It was further found (Belfort et al., 1984) that for activated carbon adsorption, ΔG_{vdw} (the dominant counteracting force) is also proportional to TSA. Thus, the difference in free energy change ($\Delta G_{vdw} - \Delta G_{cav}$) is also proportional to TSA. TSA therefore presents a means to greatly simplify the theory and it was indeed found by Belfort et al. (1984) that adsorption of alcohols and ketones by activated carbon correlates very well with both $\Delta G_{net}/RT$ as well as TSA.

The equilibrium effects of a reverse osmosis process can be described as a partitioning of the solute between the membrane phase and the solution phase. The mechanism involved in the equilibrium process can be (a) sorption of solute onto active sites on the membrane surface (large molecules which are sterically hindered to enter the membrane) or, more likely for the small molecules considered here, sorption on the micro-porous surface area of the membrane or (b) dissolution of the solute into the continuous membrane phase which implies that the solute molecule is relatively less fixed to a specific site in the membrane than molecules that are sorbed. These mechanisms can both be described by the solvophobic theory, so irrespective of the mechanism adopted the equilibrium effect can be accounted for by the solvophobic theory, ΔG_{net} or by the simplified theory, TSA. (The simplified theory does not hold for interactions between cellulose acetate membranes, with a relatively strong polar character, and polar solutes. These polar interactions must be accounted for by the comprehensive theory).

The kinetic effect can be related to diffusion across the membrane of solute molecules sorbed onto or dissolved in the membrane. Diffusion can proceed either in a "free" or "hindered" mode. Free diffusion takes place unhindered under the driving force of the chemical potential across the membrane and is applicable in the case where solute is dissolved in the membrane. However, if solute is adsorbed on the micro-porous structure of the membrane, diffusion is hindered by adsorbed molecules which reduce the avenues or corridors available for diffusion.

In Fickian diffusion the rate of solute diffusion is given by

$$J_i = -D_i \left(\frac{dC_i}{dx} \right) \dots\dots\dots 4.113$$

where D_i is the diffusion coefficient, which is determined by the size and hydrodynamic shape of the diffusing molecule and by the forces of interaction between the diffusing molecule and the membrane material. These latter forces should be accounted for by the solvophobic theory which also accounts for the effect of the size of the molecule. However, although the hydrodynamic shape of the molecule is related to surface area, an additional factor must be incorporated to account for the shape of the molecule.

A simple way to incorporate differences in diffusion rate as a result of differences in hydrodynamic shape would be to use a factor based on the ratio of cross sectional areas. The cross-sectional area of linear normal alcohols can be used as reference for aliphatic compounds and be assigned value of 1. Similarly, the cross-sectional area of the benzene molecule may be used as reference for aromatic compounds with a value of 1.

The factor for single-branched compounds such as 2-butanol and for double-branched compounds such as 2-methyl-2-propanol can be determined in a number of ways. Simply based on the number of carbon or oxygen atoms in the cross-section of the molecule, these factors would be 2 and 3 respectively. However, the ethyl group has a smaller front than double that of a methyl group, since the ethyl group contains fewer hydrogen atoms than two ethyl groups. Furthermore, since molecules are not rigid structures they will tend to assume the smallest cross-sectional area to minimize resistance to diffusion. In view of these considerations it would appear that a factor simply based on the sum of carbon and oxygen atoms in the molecule front will not be appropriate. Alternatively, the mathematical analogy to obtain a value for a combination of elements from their sum may be used *viz.*, $\sqrt{A_0} = \sqrt{A_1 + A_2 + \dots + A_n}$ which in this case would mean a factor of $\sqrt{2}$ for single-branched molecules and $\sqrt{3}$ for double-branched molecules.

The transport of solute through a relatively non polar reverse osmosis membrane such as an aromatic polyamide membrane should therefore be represented by the total cavity surface area corrected by the factor accounting for the difference in cross section area such that

$$\ln J_s \propto (\text{TSA}) \times \frac{\sqrt{A_{xs}}}{A_{xn}}$$

$$\text{or } \ln J_s = \phi + \zeta \sqrt{A_{xs}} (\text{TSA}) \dots\dots\dots 4.114$$

where ϕ and ζ are constants for a particular membrane, A_{xs} is the cross sectional area of the solute under consideration and A_{xn} is the cross sectional area of the linear equivalent of the molecule, as discussed above.

This very simple predictive model which relates solute transport (or rejection) to the total cavity surface area and a ratio factor is tested against experimental data in Section 4.6.4.

4.4 EXPERIMENTAL WORK

4.4.1 Introduction

The experimental work on rejection of organics by reverse osmosis membranes was conducted by the author in the Department of Chemical Engineering and Environmental Engineering, Rensselaer Polytechnic Institute, Troy, NY during the period January-December 1984 as visiting research scholar. The scope of these studies was limited by the time available and by the membranes that could be obtained. It was consequently decided to study in detail only two series of organic solutes viz. a series of alcohols and a series of phenols rather than to try to cover a wider spectrum of organics in less detail. The reasons for this selection are given in Section 4.4.5.

4.4.2 Equipment

4.4.2.1 Membranes. All the laboratory work was done on

- (i) A composite membrane (FT-30, Filmtec Corp., Minneapolis, MN) consisting of a very dense cross-linked aromatic poly-amide skin of 0,2 micron thickness on a 35 micron polysulphone support membrane.
- (ii) The polysulphone membrane used as support membrane for the FT-30 composite membrane.
- (iii) An asymmetric cellulose acetate membrane with high NaCl rejection, (SEPA 99, supplied by Osmonics Inc., Minnetonka, MN).

4.4.2.2 Reverse osmosis test unit. The test unit was equipped with four stainless steel high pressure test cells which could be operated in series or either one or more could be bypassed. The test cells were 48 mm in diameter and flow was across the membranes (see Figure 4.6). The flow rate could be controlled by the flow control valve between 0,5 and 8 ℓ/min. The unit could be operated at steady operating pressures in the range 550 - 6900 kPa (80-1000 psi). Operation was in the recycle mode, i.e. the feed-reject solution as well as permeate were recycled to the plastic feed reservoir. Samples of feed and product were taken at regular intervals but the volume of samples were small (50 ml) compared to the total volume in the system (about 100 ℓ).

A schematic of the test loop is shown in Figure 4.5 and of a test cell in Figure 4.6.

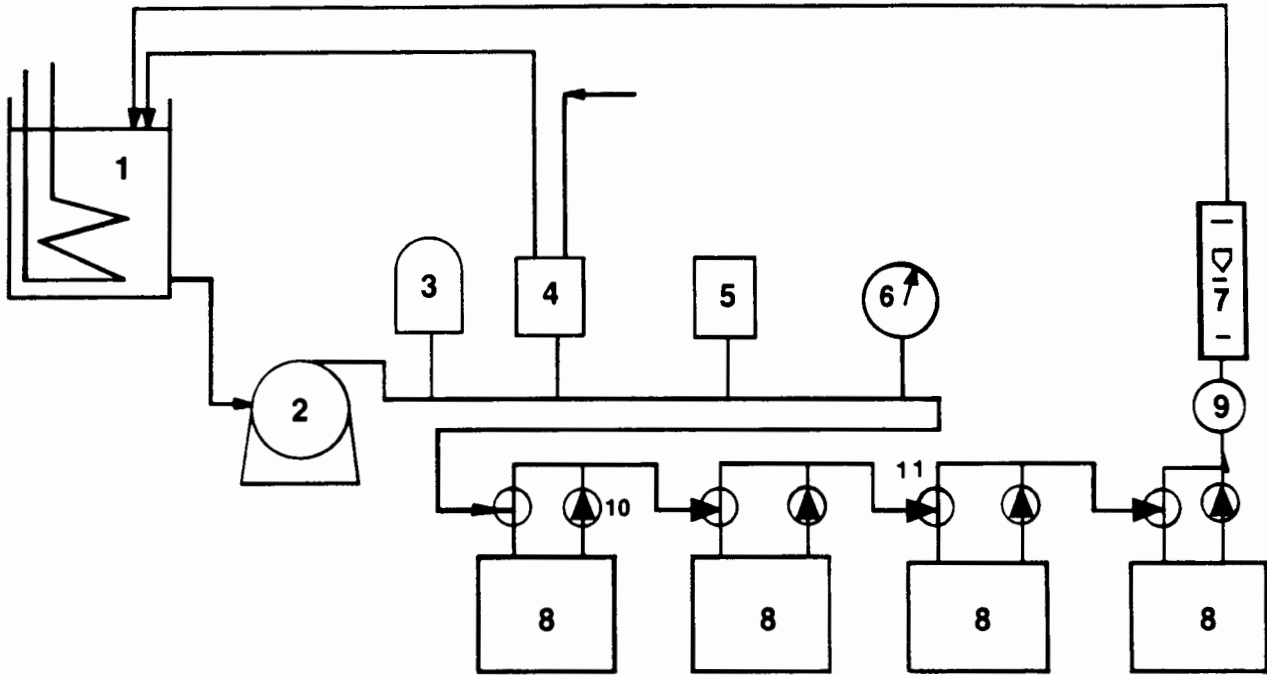
4.4.2.3 Diffusion cell. The diffusion cell consisted of two magnetically mixed chambers (filled volume 41 mℓ) separated by the membrane being tested (exposed surface area 7.07 cm²) held between two spacers. Each chamber was surrounded by an outer chamber through which constant temperature water was circulated.

A schematic of the cell is shown in Figure 4.7.

4.4.3 Test procedures

4.4.3.1 Reverse osmosis test procedures. Circular pieces of membrane (slightly larger than the cell O-ring) were cut from the membrane sheets and inserted in the test cells. The performance of membranes is affected by the "history" of operation. Different results were found for rejection and fluxes at a particular pressure depending on whether the membranes were first operated at lower pressure and then at higher pressure or vice a versa.

The same procedure was therefore followed for all the test runs in order to minimize these effects. All new membranes were at the start of a run, "stabilized" by operating with pure water (de-ionised, ultra-filtered 10 000 Daltons) at 5620 kPa (800 psi) for 3 hours. After this stabilization or compaction period pure water fluxes were determined at different pressures (usually in descending order) of 5620, 4216, 2810 and 1405 kPa (800, 600, 400, 200 psi). This also allowed screening of the membranes so that membranes with imperfections could be replaced.



1. FEED SOLUTION RESERVOIR WITH COOLING COILS
2. WANNER DIOAB PUMP
3. ACCUMULATOR
4. BACK PRESSURE REGULATOR
5. HIGH-LOW PRESSURE CUTOUT
6. 0-1500 PSI PRESSURE GAUGE
7. FLOW METER
8. TEST CELLS
9. NEEDLE VALVE FOR FLOW CONTROL
10. 2 WAY VALVES
11. 3 WAY VALVES

FIGURE 4.5: SCHEMATIC DIAGRAMME OF REVERSE OSMOSIS TEST SYSTEM

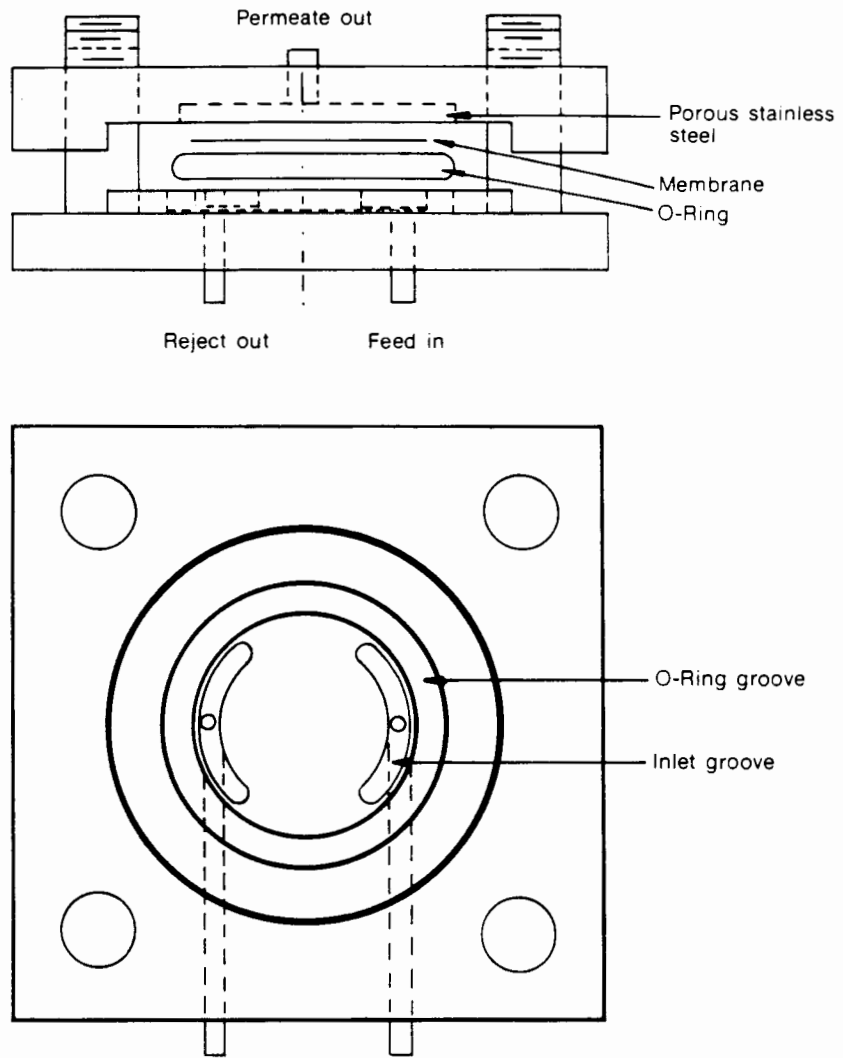


FIGURE 4.6: REVERSE OSMOSIS TEST CELL

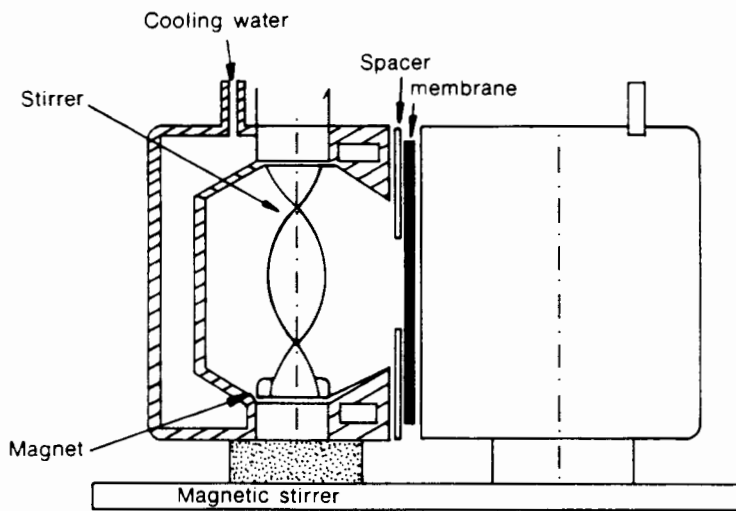


FIGURE 4.7: DIFFUSION CELL

Single-solute solutions were prepared by mixing pre-weighed quantities of pure solute (>99.0% purity) in deionised ultrafiltered water in the covered feed tank. Feed samples were taken at the start of a run and at regular intervals during the run to coincide with sampling of permeate and reject. Permeate and reject were continuously recycled to the feed reservoir so that only minor changes in feed concentrations were recorded. Extreme care had to be taken when volatile solutes were used to ensure that losses were limited. Where possible samples for analysis were taken at the cell outlet and analysed immediately.

Since heat is added to the feed by the high pressure pump and this is recycled to the feed tank it was necessary to cool the feed reservoir. This was done by circulating cooling water through a cooling coil in the feed tank to keep the temperature at $25 \pm 1^\circ\text{C}$.

The unit was operated for at least two hours for equilibrium to be established after any change in the operating conditions i.e. change in operating pressure or change in feed concentration. Membranes were replaced after each run with a particular solute before a new solution was introduced. One of the four test membranes was, however, not replaced, in order to determine the effect of different organics on rejection and flux over an extended period of time.

4.4.3.2 Partitioning/sorption test procedures. Since the amount of membrane material relative to membrane surface area in reverse osmosis membranes is very small and also because the amount of solute sorbed by the membrane materials is relatively small, accurate determination of the amount of organics sorbed is difficult. In order to get as much membrane as possible in contact with a relative small volume of solute long pieces of membrane were rolled and placed in test tubes filled with the solution of interest.

Some of the membranes contained residual chemicals which gave falsely high readings in initial tests. All the membranes were therefore washed in deionised water until most chemicals were leached out before any adsorption tests were initiated.

Membranes were placed in solutions of different concentrations, and changes in concentration of the solutions were monitored until equilibrium was reached. Samples removed for ultraviolet spectrophotometric determination of concentration were returned to maintain a constant volume.

It was not possible to separate the FT-30 polyamide skin from the understructure. The amount sorbed by the skin was therefore determined from the difference between the amount sorbed by the FT-30 membrane and that sorbed by the polysulphone support membrane.

A second set of tests monitored adsorption and desorption independently from both the skin and porous sides of the membranes when placed in the diffusion cell.

The temperature was controlled at $25 \pm 2,5^{\circ}\text{C}$.

- 4.4.3.3 Diffusion test procedures. Membranes used in the diffusion tests were also washed in de-ionised water to remove unreacted chemicals. A circular piece of membrane was placed between the two spacers between the chambers of the diffusion cell. Pure water was put in one chamber and the solution of interest in the other chamber at the skin side of the membrane. The increase in concentration in the pure water chamber was then monitored at intervals of 2 minutes until a steady rate of increase was maintained. Samples removed for ultraviolet spectrophotometric determination of concentration were returned to maintain a constant volume.

Temperature was controlled at $25 \pm 0,25^{\circ}\text{C}$.

4.3.4 Analytic Procedures

Sodium chloride concentrations were determined using a Beckman model 39093 conductivity cell. The concentration of aromatic compounds was determined with a Perkin-Elmer spectrophotometer Model 552, while alcohol concentrations were determined by total organic carbon analysis in a model 915A Beckman CA. TOC analyser.

8.4.5 Solutes

Two series of solutes were selected for the study i.e. a series of alkyl alcohols and a series of alkyl phenols, as well as a number of individual solutes including benzene, toluene, acetone and cyclohexane.

(i) Alcohols

methanol; ethanol; 1-propanol; 2-propanol; 1-butanol; 2-butanol; 2-methyl-1-propanol; 2-methyl-2-propanol; 1-pentanol; 1-hexanol; 1-heptanol.

This series of alcohols was chosen because they are relevant in water pollution control since some of them are used as industrial solvents and some are by-products of biological degradation processes. In addition most of their physical chemical characteristics are available in the literature and their concentration can be relatively easily and accurately determined. Further, numerous studies on the performance of cellulose acetate membranes on these alcohol solutions are reported in the literature which can be used as a basis of comparison.

(ii) Phenols : phenol; 4-methyl phenol; 4-ethyl phenol; 2, 6 - dimethyl phenol; 4-n-propyl phenol; 4-isopropyl phenol; 4-n-butyl phenol.

Phenols were chosen as test solutes because they are present in many industrial wastewaters and their concentration can be very easily and very accurately determined. Further, it is also well known that phenols are poorly rejected by cellulose acetate membranes. The physical-chemical characteristics of these compounds are well documented.

4.5 MEMBRANE CHARACTERIZATION

4.5.1 Introduction

In order to relate the organic rejections and fluxes of membranes to their performances with respect to sodium chloride an initial series of characterization tests was conducted. This included the determination of pure water fluxes under different operating pressures as well as rejections and fluxes with different sodium chloride solutions (2 500, 10 000, 20 000, 30 000 mg/ℓ).

From these data the following membrane characteristics are derived :

- (i) Phenomenological coefficient L_p ; Solution-diffusion constant A .
- (ii) J_v , total volume flux as a function of applied pressure difference ($\Delta P - \Delta \pi$).
- (iii) R_i , rejection coefficient as a function of ΔP and ($\Delta P - \Delta \pi$) and of the concentration difference (C_f and C_p).
- (iv) R_{max} .

In Section 4.6 reverse osmosis, adsorption and diffusion data for the alkyl alcohols and phenols are given.

4.5.2 Pure Water Flux and Solvent (Water) Flux

Pure water permeation rates were determined using stabilized membranes and de-ionized ultrafiltered feed water.

Pure water flux and solvent (water) flux in general are subject to change with time as a result of "compaction" (and in practical applications due to membrane fouling). The term "compaction" refers to a densification of the whole membrane (skin and porous support) resulting in reduced flux and improved solute rejection. This phenomenon is explained as a "densification" of the membrane which means that the pores or voids are reduced in size or alternatively that the polymer structure is compressed thus reducing the rate of diffusion through the membrane. This is also reflected by higher solute rejection at higher pressures than at lower pressures. However, in the latter case the argument is advanced that rejection is a function of water flux and increases with increased flux i.e. solvent flux increases more rapidly than solute flux (which is a function of the concentration difference across the membrane).

Pure water flux of a membrane decreases rapidly in the beginning (during the first few hours of operation) and then stabilizes. However, flux reduction continues throughout the lifetime of the membrane but at a much lower rate. When membranes are depressurized a certain degree of relaxation occurs so that compaction again occurs when the membrane is pressurized. Figure 4.8 shows typical pure water fluxes for the FT-30 and SEPA-99 membranes as a function of time at 5620 kPa.

The range of fluxes found in this study is shown in Figure 4.9 for new membranes stabilized at 5620 kPa for 2 hours. The flux of one FT-30 membrane which was in the test cell over a period of 3 months and about 250 hours of operation and which has seen different alcohol and phenol solutions is also shown in Figure 4.9.

From $J_v = L_p (\Delta P - \sigma \Delta \pi)$

$$J_v = L_p \Delta P \quad (\Delta \pi = 0 \text{ for pure water})$$

$$L_p = 7,12 \times 10^{-7} \text{ cm/s.kPa} \quad - \text{ New FT-30 membrane}$$

$$L_p = 6,41 \times 10^{-7} \text{ cm/s.kPa} \quad - \text{ FT-30 membrane after 250 hours}$$

$$L_p = 1,25 \times 10^{-7} \text{ cm/s.kPa} \quad - \text{ SEPA-99 membrane}$$

The water flux through the polysulphone ultra-filtration membrane could not be accurately determined because the lowest operating pressure of the test unit was still very high for the membrane.

A typical flux value at 562 kPa (80 psi) is about $110 \text{ cm/sec} \times 10^{-4}$ (200 gfd)

This gives $L_p = \frac{110}{562} = 1,96 \times 10^{-5} \text{ cm/s.kPa}$

4.5.3 Sodium Chloride Data

Water flux and rejection data for NaCl solutions were collected at different concentrations viz. 2 500, 10 000, 20 000, 30 000 mg/ℓ and are given in Table 4.1 and shown in Figures 4.10, 4.11 and 4.12.

In Figure 4.10 J_v is plotted against $(\Delta P - \Delta \pi)$ for 2 500 mg/ℓ NaCl solutions and the FT-30 and SEPA-99 membranes respectively. The same data for the FT-30 membrane and different NaCl concentrations are plotted in Figure 4.12 (values for the osmotic pressure at different concentrations were taken from Spiegler and Laird, 1980) and in Figure 4.11 J_v is plotted against the operating pressure. Water fluxes for the different solutions can be extrapolated to zero flux at a pressure very close to the calculated osmotic pressure. However, in practice flux through the membrane could not be stopped completely by lowering the operating pressure to even below the extrapolated or theoretical osmotic pressure values. Very low fluxes which could not be measured but could be observed visually continued at pressures as low as 1054 kPa(150 psi) at 20 000 mg/ℓ NaCl. This indicates that some "leakage" albeit very small occurred. The nature of this leakage is difficult to determine but a plausible explanation may be that it is caused by convective flow through some imperfection in the membrane.

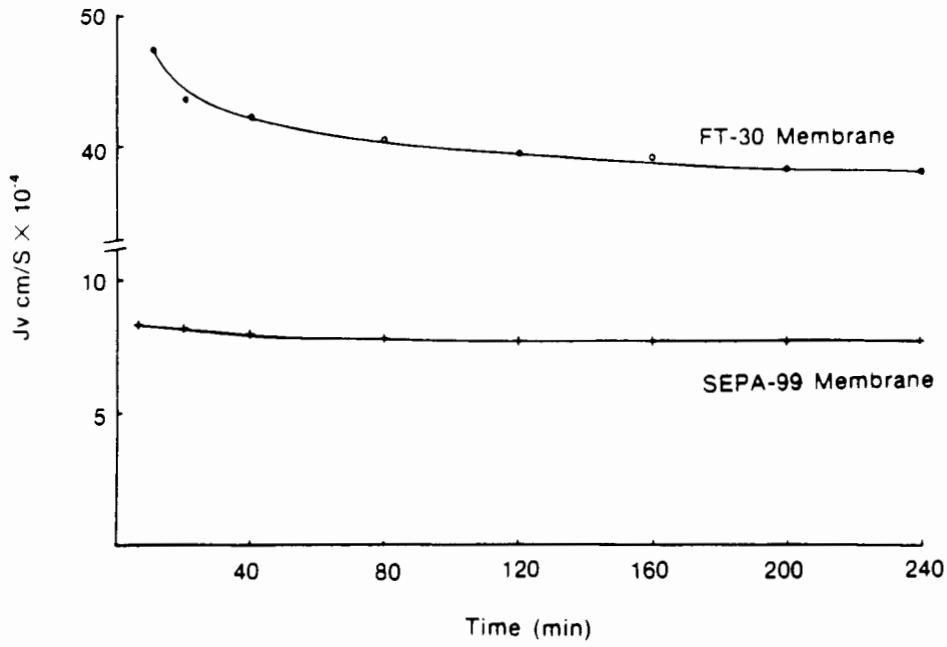


FIGURE 4.8: PURE WATER FLUX vs. TIME AT 5620 kPa

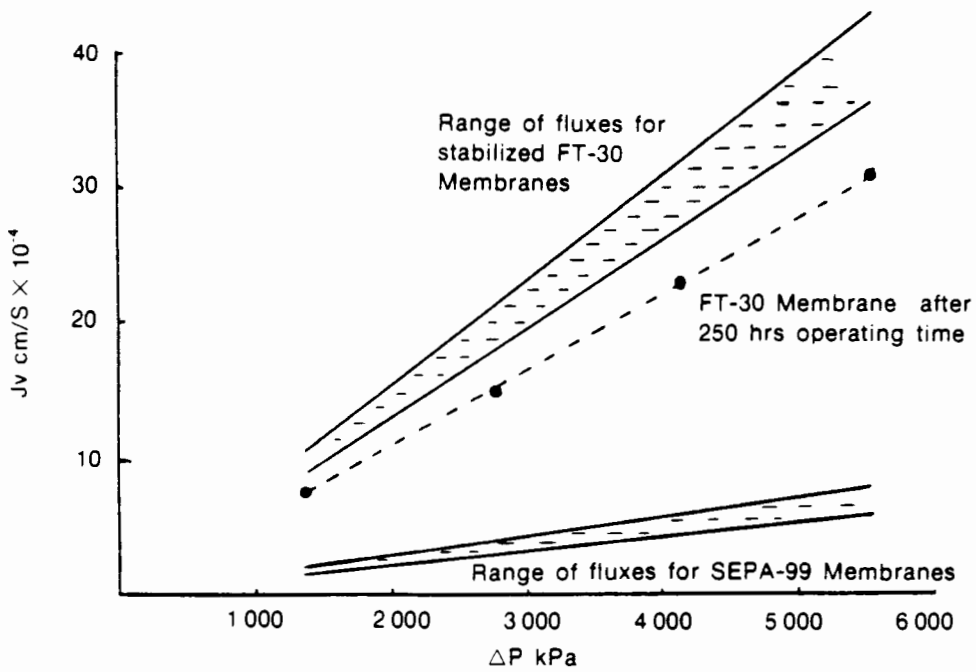


FIGURE 4.9 : PURE WATER FLUX (Jw) vs OPERATING PRESSURE (ΔP)

TABLE 4.1 : WATER FLUX AND REJECTION DATA FOR NaCl FEED SOLUTIONS AND FT -30 AND SEPA - 99 MEMBRANES

FEED CONC.	PARAM.	MEMBRANE	ΔP (kPa)			
			5620	4210	2810	1405
NaCl (mg/l)						
2500 ($\pi = 199$ kPa)	R	FT 30	0,995	0,994	0,993	0,983
		SEPA	0,990	0,986	0,979	0,970
	Jv cm/S $\times 10^{-4}$	FT 30	33,0	24,8	16,7	8,5
		SEPA	7,0	5,1	3,5	1,8
10 000 ($\pi = 793$ kPa)	R	FT 30	0,993	0,992	0,986	0,972
		FT 30	31,2	21,0	12,4	3,9
20 000 ($\pi = 1586$ kPa)	R	FT 30	0,994	0,992	0,986	-
		FT 30	21,2	13,4	6,6	-
30 000 ($\pi = 2379$ kPa)	R	FT 30	0,992	0,989	0,981	-
		FT 30	12,1	7,2	2,1	-
	Jv cm/S $\times 10^{-4}$					

4.61

Lp for the different NaCl solutions from Figures 4.10 and 4.11 are :

$$\begin{aligned} L_p (2\ 500) &= 5,9 \times 10^{-7} \text{ cm/s.kPa} \\ L_p (10\ 000) &= 6,5 \times 10^{-7} \text{ " } \\ L_p (20\ 000) &= 5,2 \times 10^{-7} \text{ " } \\ L_p (30\ 000) &= 3,7 \times 10^{-7} \text{ " } \\ L_p (\text{pure water}) &= 7,1 \times 10^{-7} \text{ " } \end{aligned}$$

The values for Lp (or A) for the same membrane should remain constant for different salt concentrations but in this case varied especially for the higher concentrations. The Jv vs ($\Delta P - \Delta \pi$) relationships however remain linear even at the highest concentrations. A possible explanation for the variation in A values is that they were affected by fouling of the membranes. This was confirmed by the fact that corrosion occurred somewhere in the test system at the high NaCl concentrations and that the corrosion products fouled the membranes thus causing additional hydraulic resistance and affecting the values of A. This was confirmed by inspection of the membranes after the tests which showed a brownish fouling layer on all the membranes. The additional resistance to flow was also demonstrated by the reduction in flux when the NaCl feed was replaced by pure water. The membranes were just flushed without chemical cleaning and the pure water fluxes determined. The pure water fluxes are shown in Table 4.2.

TABLE 4.2. PURE WATER FLUX AFTER NaCl RUNS :
FT-30 MEMBRANE

ΔP kPa	5620	4216	2810	1405
Jv. cm/s $\times 10^{-4}$	31,9	23,4	15,5	8,0

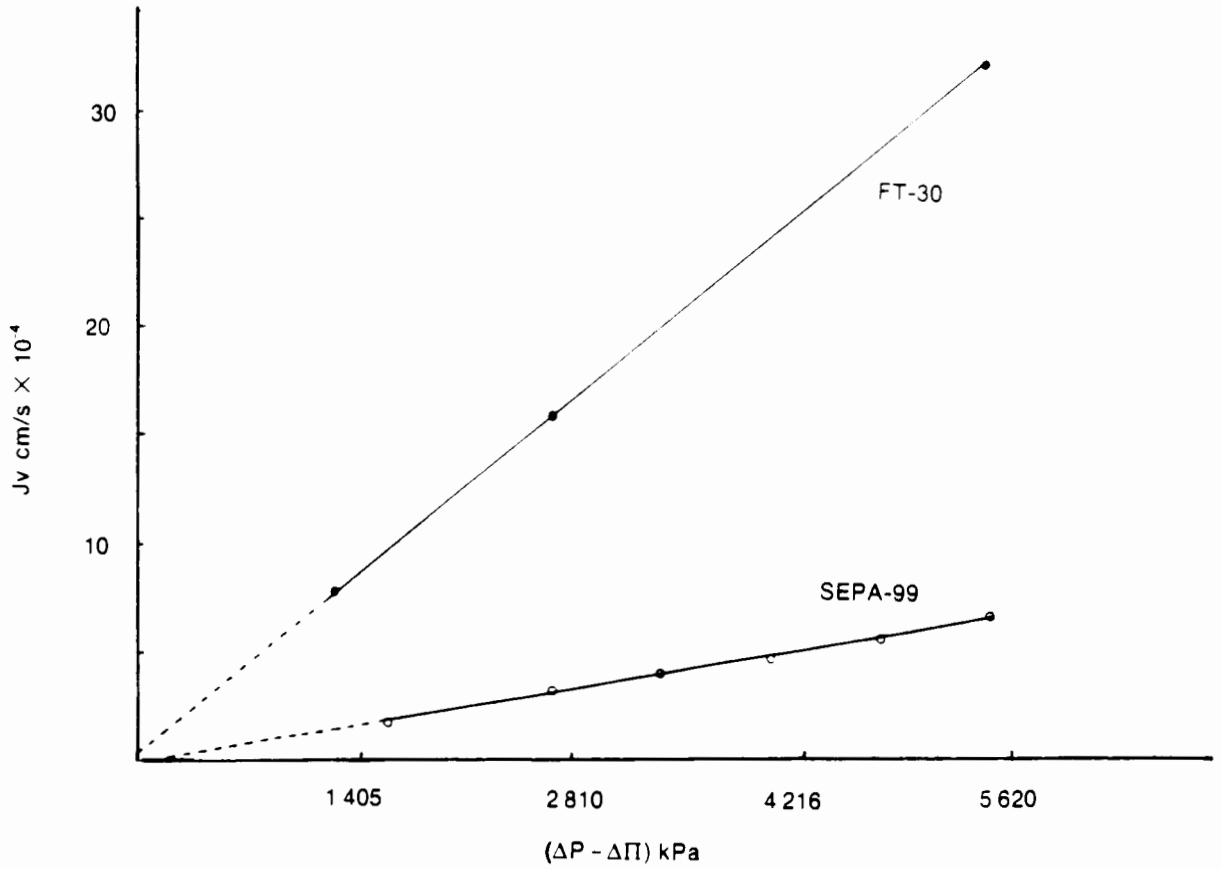


FIGURE 4.10 WATER FLUX vs. EFFECTIVE PRESSURE; 2 500 mg/l NaCl FEED

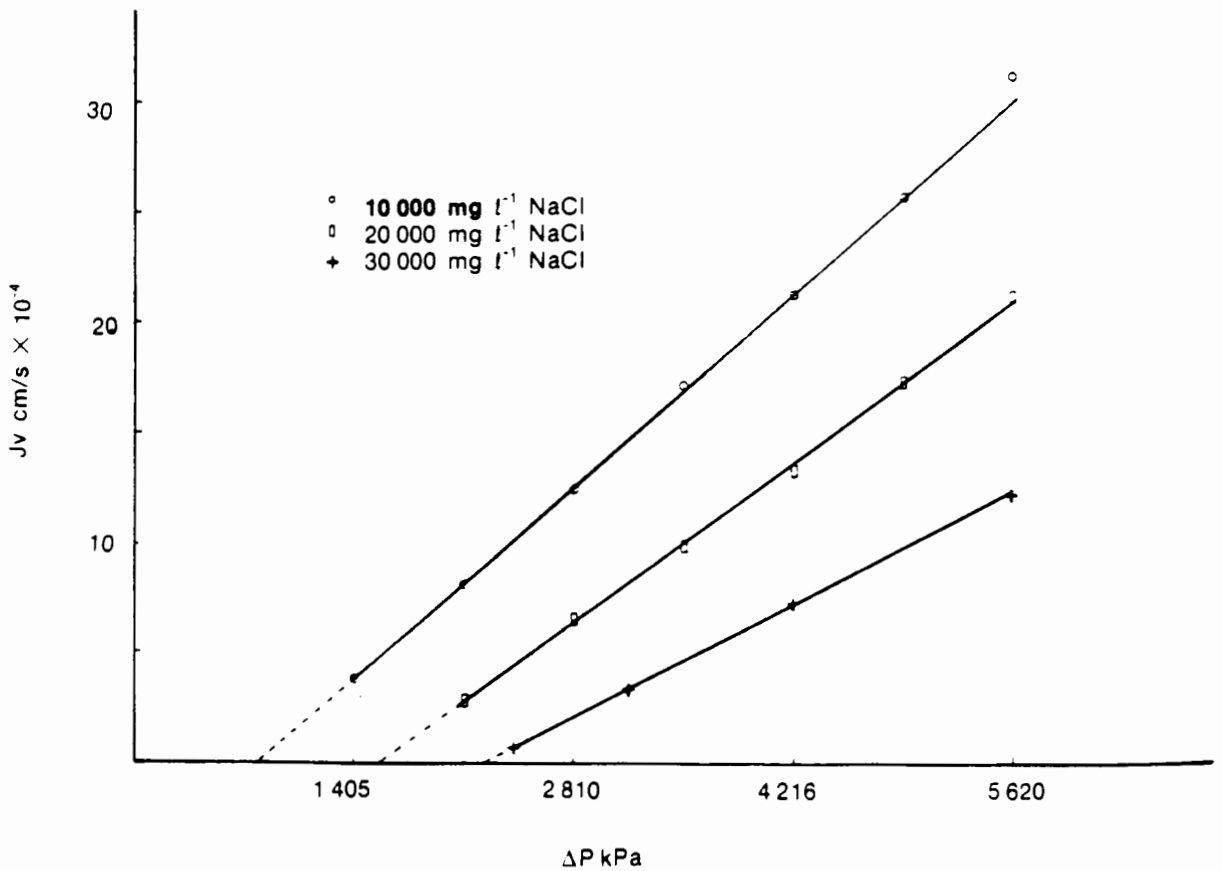


FIGURE 4.11: WATER FLUX vs. OPERATING PRESSURE; NaCl FEED SOLUTIONS; FT-30 MEMBRANE

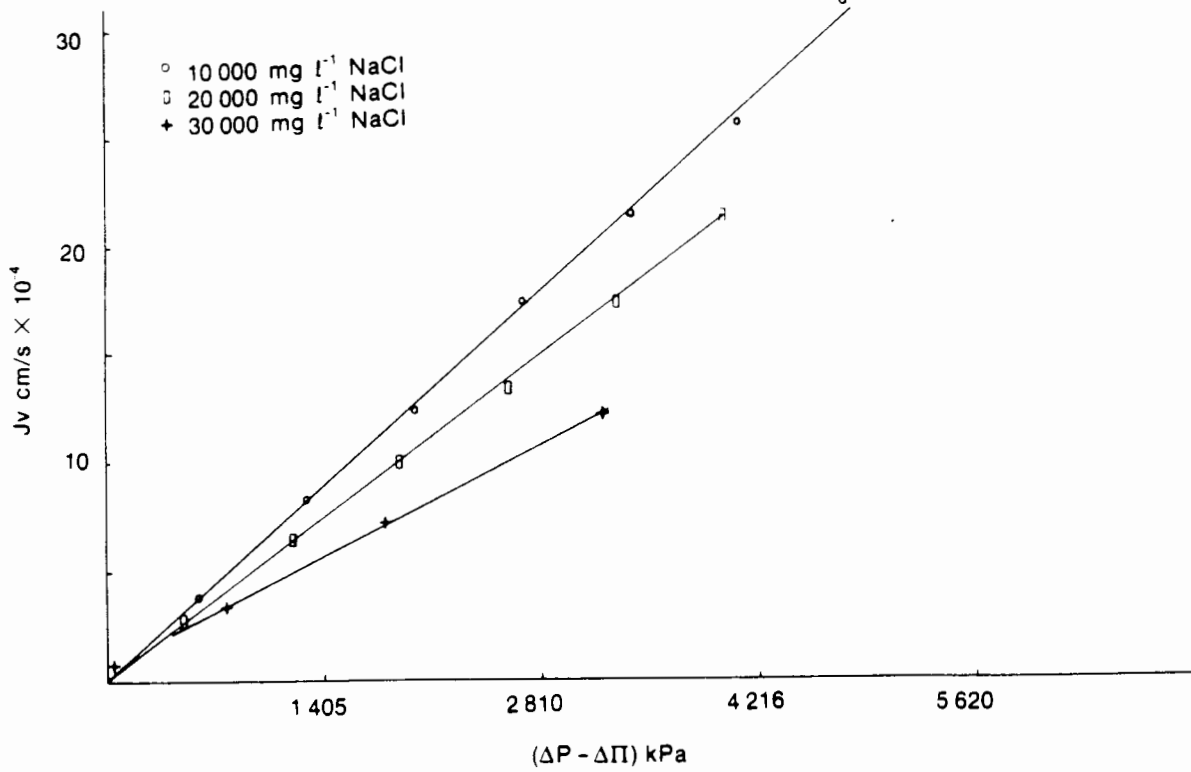


FIGURE 4.12: WATER FLUX vs EFFECTIVE PRESSURE; NaCl FEED SOLUTIONS FT-30 MEMBRANE

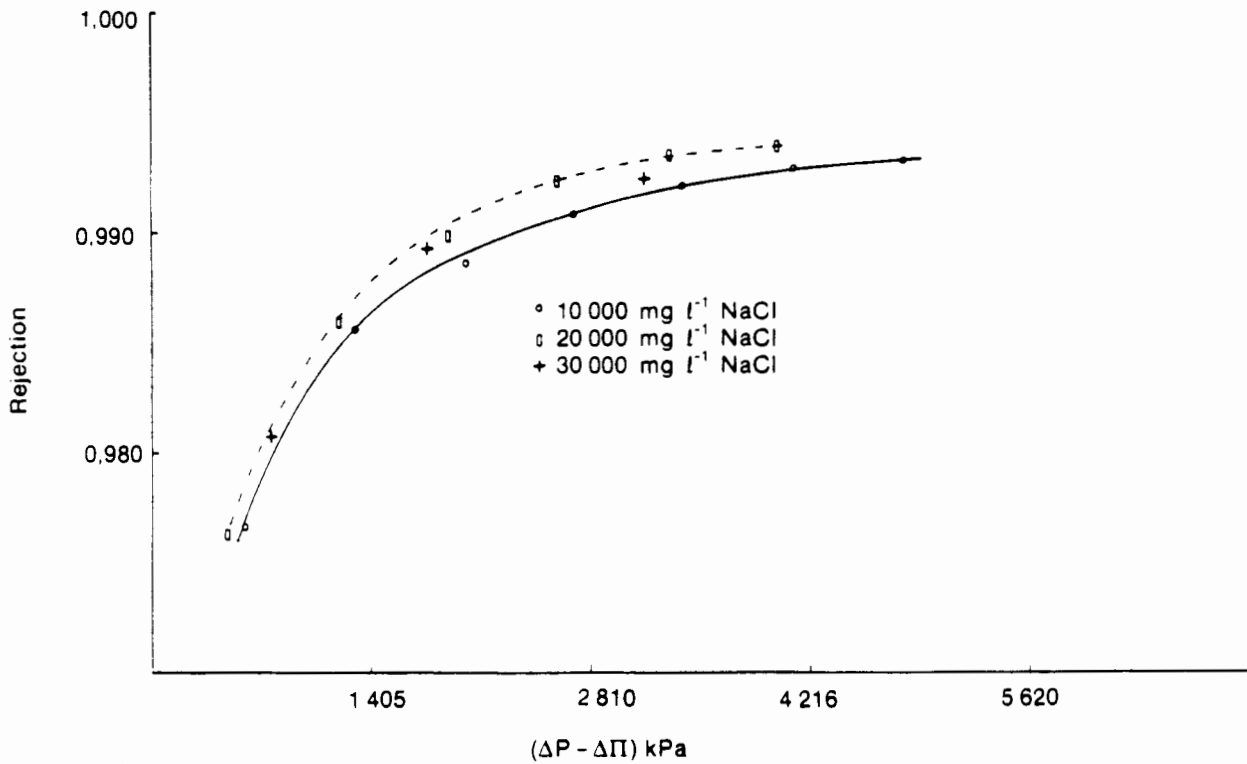


FIGURE 4.13: NaCl REJECTION vs. EFFECTIVE PRESSURE; FT-30 MEMBRANE

The additional resistance to flow caused by the fouling layer caused a reduction in flux from 64×10^{-4} down to 32×10^{-4} cm/s at 5620 kPa accounting for the decrease in the value of L_p at the different NaCl concentrations.

The dependence of salt rejection on effective pressure ($\Delta P - \Delta \pi$) is shown in Figure 4.13. It is evident that the fouling which occurred had very little effect on salt rejection and that its effect was limited to flux reduction.

The rejection increases sharply from a low of 0,977 at an effective pressure of about 500 kPa and asymptotically approaches maximum rejections of 0,990 to 0,993 at pressures higher than about 4 000 kPa.

The effect of pressure on salt rejection may also be illustrated in a different manner.

From $J_v = A(\Delta P - \Delta \pi)$ it follows that

J_v is linearly related to $(\Delta P - \Delta \pi)$ and the effect of pressure can therefore be demonstrated by relating R to J_v .

Pusch (1977) showed the relationship between J_v and R to be as follows

$$1/R = 1/R_x + (L_D/L_P - R^2)L_P\pi_R/R_x \cdot 1/J_v \quad \dots\dots\dots 4.115$$

where R_x is the maximum rejection obtainable.

A plot of $1/J_v$ vs $1/R$ should therefore give a straight line with R_x at $1/J_v = 0$. Plots of $1/J_v$ vs $1/R$ are shown in Figure 4.14 for different NaCl concentrations and FT-30 membranes, and in Figure 4.15 for 2 500 mg/l NaCl and FT-30 and SEPA-99 membranes. The FT-30 membrane with its high water flux gives straight lines for all concentrations with R_x values ranging between 0,996 and 0,998. The differences in slope and in position can again be ascribed to the additional resistance to flow at the higher concentrations as a result of fouling.

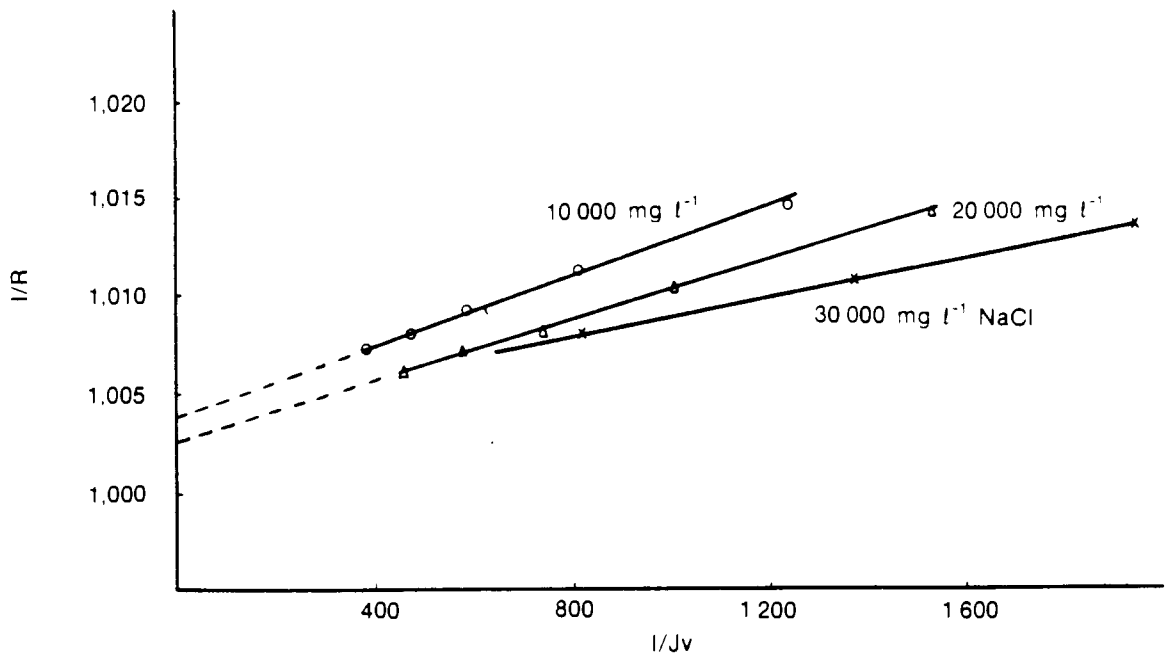


FIGURE 4.14: 1/Jv vs. 1/R; NaCl FEED SOLUTIONS; FT-30 MEMBRANE

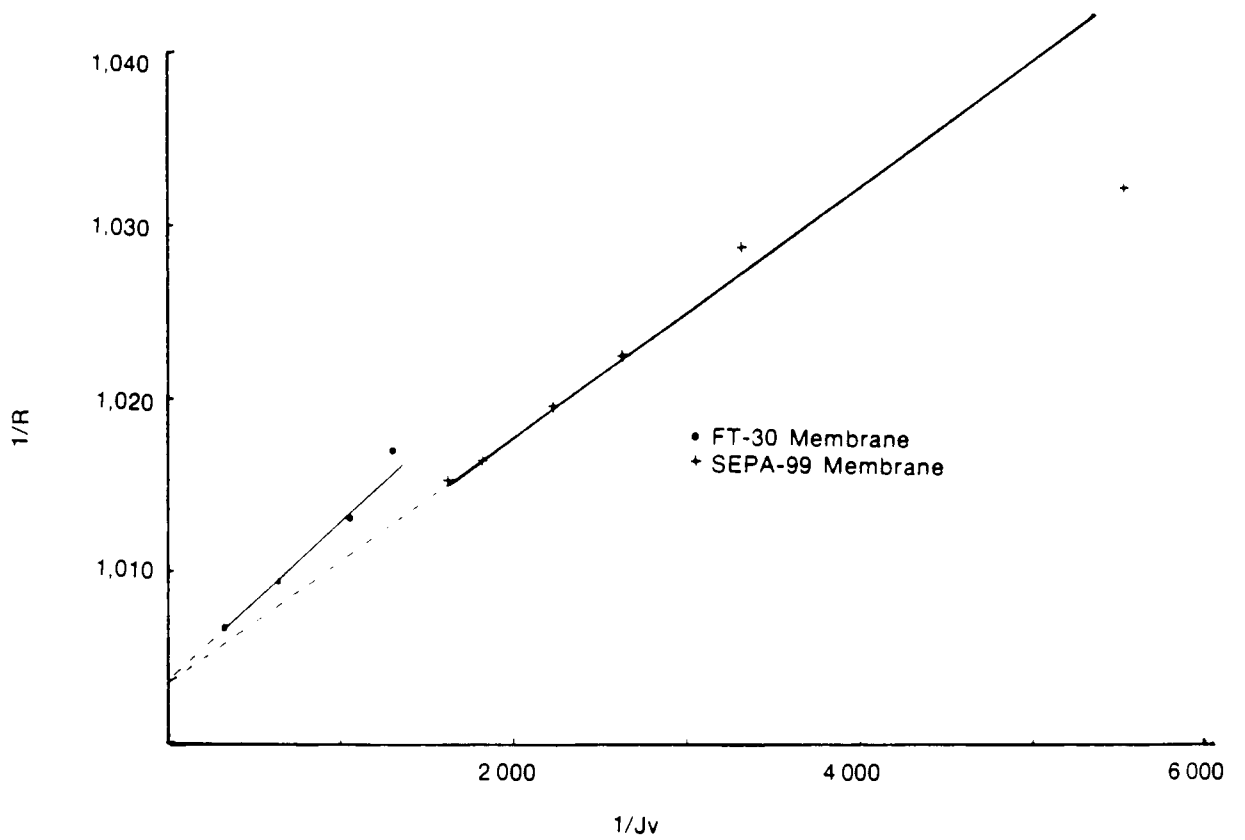


FIGURE 4.15 1/Jv vs. 1/R; 2 500 mg l⁻¹ NaCl

The SEPA-99 membrane has a much lower hydraulic permeability but still gives a reasonably straight line plot for $1/J_v$ vs $1/R$ with $R_x = 0,99$.

4.6 EXPERIMENTAL DATA FROM ALCOHOL AND PHENOL TESTS

4.6.1 Introduction

Three separate sets of tests were conducted i.e. reverse osmosis tests on the two series of alcohols and phenols mentioned in Section 4.4 using the cellulose acetate and composite aromatic polyamide membranes; sorption tests focussing on phenol; and diffusion tests also using phenol solutions. Data from the sorption and diffusion tests are necessary to evaluate the solution-diffusion and related transport models.

Reverse osmosis tests were conducted using a range of feed concentrations for different solutes and over a range of operating pressures from 5620 kPa to 1405 kPa (800-200 psi). Some of the solutes were studied in more detail with respect to the effect of feed concentration, while in other tests pressure effects were investigated in more detail.

4.6.2 Reverse osmosis data

Reverse osmosis tests were conducted using the procedures described in Section 4.4.3.1. Water flux and rejection data for these tests are given in Appendix B. Tables B1-B11 give data on the alcohols tested and Tables B12-17 give the same data for the phenols.

Tables 4.3 and 4.4 summarize alcohol and phenol rejection data respectively while Figure 4.16 graphically shows alcohol rejection by the two membranes as a function of molecular mass. It is evident from this figure that there is a well defined pattern for the rejection of the linear homologues by the FT-30 membrane as shown by the

line connecting the different rejection points. On the other hand rejection of the linear homologues by the cellulose acetate membrane is much lower and does not follow the same pattern of higher rejection for higher homologues. Maximum rejections of 25-30% are obtained for methanol and 1-propanol while rejection of 1-hexanol, for example, is much lower at about 10%.

The general trend of rejection of linear alcohols by the FT-30 membrane indicates that a simple correlation exists with molecular mass. However, rejection of the branched isomers does not fall into this pattern. It should be noted that rejection of branched isomers is markedly higher than for linear isomers of equal molecular mass. For the rejection of alcohols by the composite aromatic polyamide membrane, molecular mass of the particular alcohol gives a good indication of the degree of rejection that may be attained taking into account that rejection of branched isomers will be higher than rejection of the linear equivalent.

Rejection of the different phenols by the composite membrane (Table 4.4) follows the same general trend as for the alcohols with higher rejections as the molecular mass and molecular size of the solute increase. Here again, rejection by the cellulose acetate membrane is in general very much lower than rejection by the composite membrane and even negative rejections of phenol are recorded.

A number of studies on the rejection of alcohols and phenols are reported in the literature. Gary-Bobo *et al.* (1969) studied the diffusion of some alcohols and amides through cellulose acetate membranes and found that differences in partition coefficients may, at least partially, account for differences in the permeation of different solutes.

TABLE 4.3 : ALCOHOL REJECTION DATA, DILUTE FEED SOLUTIONS 5,0 mmol/l, 25°.

Solute	FT 30 rejection			Mol mass	SEPA 99 rejection		
	1405 kPa	2810 kPa	5620 kPa		1405 kPa	2810 kPa	5620 kPa
METHANOL (1)	0,22	0,28	0,36	32,0	NA	0,094*	NA
ETHANOL (2)	0,55	0,65	0,75	46,1	0,24	0,182* 0,24	0,27
1-PROPANOL (3)	0,82	0,86	0,88	60,1	NA	0,293*	NA
2-PROPANOL (4)	0,93	0,95	0,976	60,1	NA	0,480*	NA
1-BUTANOL (5)	0,89	0,92	0,93	74,1	0,17	0,218* 0,17	0,23
2-BUTANOL (6)	0,962	0,970	0,982	74,1	NA	0,497*	NA
2-METHYL- 1-PROPANOL (7)	0,970	0,975	0,984	74,1	NA	0,497*	NA
2-METHYL- 2-PROPANOL (8)	0,983	0,990	0,994	74,1	0,80	0,868* 0,80	0,84
1-PENTANOL (9)	0,90	0,92	0,944	88,2	NA	0,185*	NA
1-HEXANOL (10)	0,93	0,94	0,955	102,2	0,11	0,155* 0,09	0,07
1-HEPTANOL(11)	0,93	0,955	0,967	116,2	NA	0,131	NA

NA = not available

*Calculated values for cellulose acetate membrane with NaCl rejection of 0,968. (Sourirajan and Matsuura 1978)

TABLE 4.4 : REVERSE OSMOSIS DATA FOR PHENOLS. DILUTE FEED SOLUTIONS
 2,0 mmol/l 25°C

Solute	FT 30 Rej. at 1405 kPa	FT 30 R at 2810 kPa	FT 30 R at 5620 kPa	Mol mass	SEPA 99 R at 1405 kPa	SEPA 99 R at 2810 kPa	SEPA 99 R at 5620 kPa
PHENOL	0,87	0,92	0,94	94,1	0,02	0	-0,04
4 METHYL PHENOL	0,91	0,94	0,967	108,1	NA	NA	NA
4 ETHYL PHENOL	0,93	0,96	0,970	122,2	NA	NA	NA
2,6 DIMETHYL PHENOL	0,975	0,978	0,991	122,2	0,44	0,31	0,20
4 n PROPYL PHENOL	0,967	0,976	0,980	136,2	0,20	0,11	0,05
4 ISOPROPYL PHENOL	0,978	0,984	0,988	136,2	0,38	0,35	0,23
(BENZENE)	0,80	0,86	0,88	78,1	NA	NA	NA
(TOLUENE)	0,84	0,90	0,94	92,2	NA	NA	NA

NA = not available

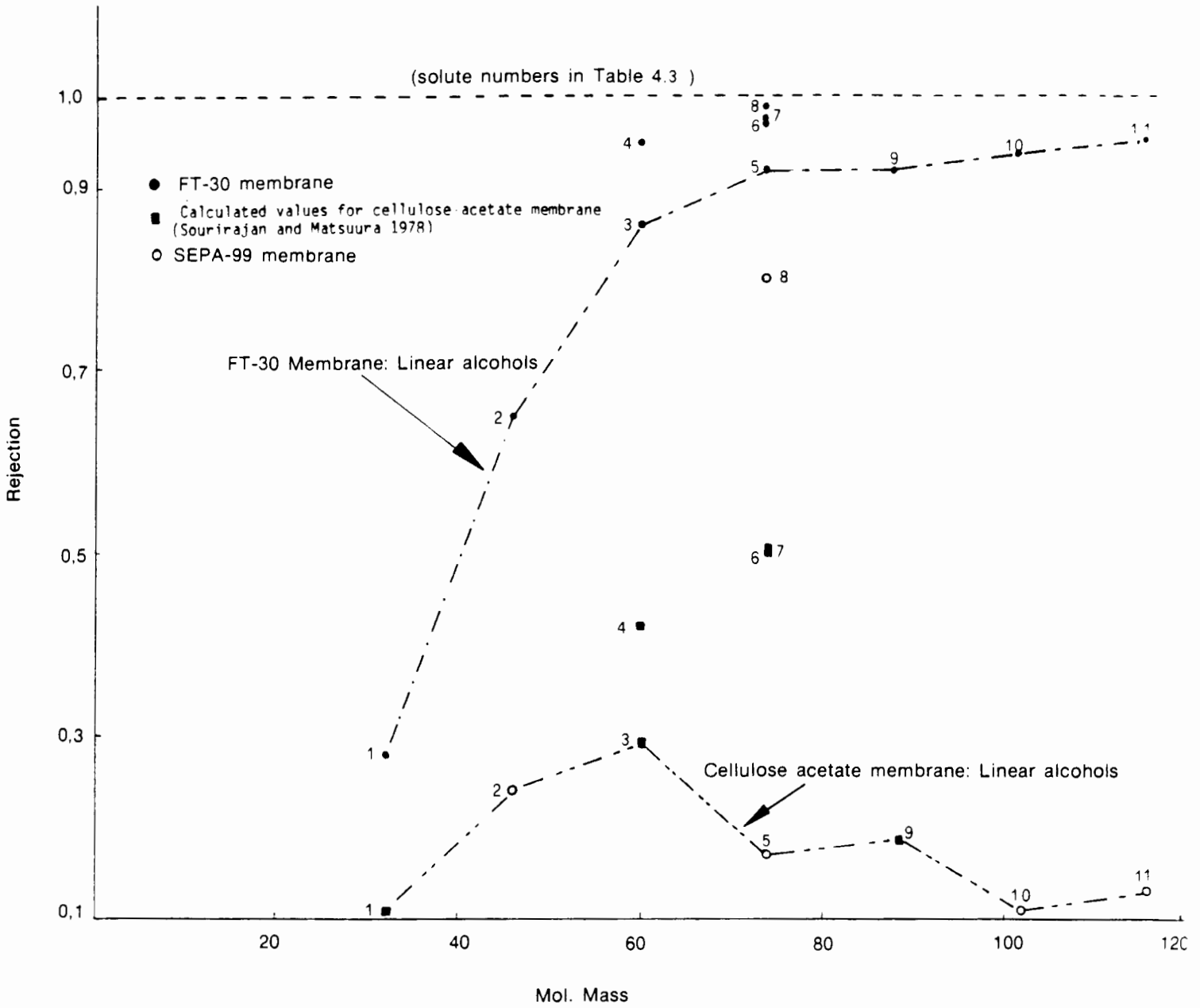


FIGURE 4.16: ALCOHOL REJECTION vs. MOLECULAR MASS

Duvel and Helfgott (1975) in a study on the rejection of a selected group of alcohols by cellulose acetate membranes found that the increase in rejection with increase in molecular weight is overshadowed by the effect of branching. They conclude that since the alcohols should have the same chemical affinity for the membrane the differences in retention are thus caused principally by differences in diffusion rates of the solute across the membrane. This assumption that all the alcohols should have the same chemical affinity for the membrane is, however, not correct since chemical affinity is not only determined by the functional group but also by the properties of the substituent group which may differ largely between a small polar molecule such as methanol and a long relatively non-polar molecule such as 1-heptanol. They found higher rejections of higher normal alcohols such as 1-heptanol (0,50) and 1-octanol (0,65) which is in contrast to the findings of this study, *viz.* that rejection by cellulose acetate membranes of higher linear alcohols is lower than for the higher homologues.

Dickson *et al.* (1975) found that reverse osmosis separation of alcohols by aromatic polyamide membranes is governed by both polar and steric parameters. This conclusion was reached from the correlation of rejection vs polar and steric parameters as expressed by

$$\ln \frac{D_{Am}}{K \delta} = \rho^* \Sigma \sigma^* + \delta^* \Sigma E_s + \ln C^* \dots\dots\dots 4.116$$

This finding appears to contradict another finding in this work i.e. that the aromatic polyamide membrane material is only about 39% as polar as the cellulose acetate membrane material. Rejection of alcohols by the less polar polyamide membrane should therefore be affected to a lesser degree by polar interactions than is the case for cellulose acetate membranes and non-polar interactions should predominate in this case.

Chian and Fang (1976) also studied the removal of alcohols and other organics by different membranes. They conclude that steric along with polar effects play a major role in separating molecules within the same functional group in all membrane materials tested by them, including cellulose acetate and aromatic polyamide.

Matsuura et al. (1977) found that rejection of normal alcohols by cellulose acetate membranes increases from methanol through 1-propanol and then decreases through 1-octanol followed by a large increase in rejection of 1-nonanol, which is similar to the findings of this study. They concluded that reverse osmosis separations by cellulose acetate membranes of dilute alcohol solutions are governed by both the polar and the non-polar character of the alcohol molecule. The initial increase in separation with increase in carbon number is, according to this view, due to the effect of the decrease in the polar character of the molecule while the subsequent decrease in rejection can be explained by the increase in the non-polar character of the molecule. As the non-polar character increases the solute molecule is drawn progressively closer to the membrane surface which eventually results in a decrease in product flux as a result of pore blocking.

Sourirajan and Matsuura (1977) explained the negative separation of phenol solutions by cellulose acetate membranes by the preferential sorption of phenol by cellulose acetate and the mobility of phenol at the solution-membrane interface. Since the cellulose acetate has a net proton acceptor nature any polar compound is attracted to the membrane surface. When the solute is more polar than the solvent the solute is preferentially sorbed by the membrane. Phenol, which is more polar than water is therefore preferentially sorbed and since water and phenol are both polar a strong interaction exists allowing the solute to be relatively "mobile" in the vicinity of the membrane pores. Thus it can be carried through the pore with the water resulting in negative separation.

Due to the hydrocarbon backbone of cellulose acetate it has a non-polar character thus also preferentially sorbing non-polar hydrocarbons. The non-polar solutes are relatively immobile at the membrane surface giving positive rejections. Both polar and non-polar preferentially sorbed solutes have a pore blocking effect due to their presence in the membrane surface which restricts the flow of the solvent water, giving severe flux reductions. This explanation for the observed flux reduction is more acceptable than an earlier theory of the transient densification of the porous structure of cellulose acetate membranes (Matsuura and Sourirajan 1971) since the same phenomenon is observed with aromatic polyamide membranes where the densification theory does not hold.

The different findings from experimental work and the different theories advanced to explain the rejection of alcohols and phenols by especially cellulose acetate membranes indicate the need for further studies in this field. The studies discussed further on in this section on the effects of different factors on rejection and flux is an attempt to improve this situation.

4.6.2.1 Effect of operating pressure on the rejection of alcohols and phenols and on water flux

The effect of operating pressure on solvent flux and rejection with feed solutions of 1-propanol, phenol, 4-n propyl phenol and 4-methyl phenol is shown in Figures 4.17 to 4.20 respectively. In all these cases water flux increases linearly with increasing operating pressure according to $J_v = A (\Delta P - \Delta \pi)$. The effect of concentration on J_v is discussed in Section 4.6.2.2 and will not be considered here.

In a particular test run data were usually collected in a descending order, starting at the highest operating pressure. This was done in order to eliminate variations that might be introduced by different compaction patterns as is discussed in Section 4.4.3.1. The series of tests on 4-methyl phenol was conducted differently by starting

at the lowest pressure, increasing the pressures and then decreasing the operating pressure again. The data in Figure 4.20 show that the water flux in this case also increased linearly with increasing pressure irrespective of the point in the sequence that the flux data were collected.

Rejection of the solutes mentioned above by the FT-30 membrane follows the same pattern viz. that the rejection increases with operating pressure, reaching an asymptotic maximum at higher pressures. However, the pattern of rejection of phenols by the cellulose acetate is different to the well-known R vs ΔP pattern since rejection in some cases decreases with increasing operating pressure. A possible explanation for the poor phenol rejection by cellulose acetate membrane and the decrease in rejection with increased operating pressure is discussed in Section 4.6.4.

The effect of operating pressure on flux and rejection with the FT-30 membrane is in accordance with general membrane theory, and the data should therefore follow the relationships that were derived in Section 4.2. For example the Pusch relationship (Equation 4.115)

$$1/R = 1/R_x + (L_D/L_P - R_x^2)L_P\pi_R/(R_x J_v)$$

which relates R to J_v should be followed. Figure 4.21 shows that this relationship is indeed valid for phenol and the FT-30 membrane. A plot of $1/J_v$ vs $1/R$ should be a straight line with a slope of $(L_D/L_P - R_x^2)L_P\pi_R/R_x$ and an intercept of $1/R_x$. As J_v becomes increasingly larger at high ΔP , the rejection reaches an asymptotic maximum value of R_x . Plots of $1/J_v$ vs $1/R$ for phenol solutions from 1,4 to 69 mmol/l give R_x values between 0,962 and 0,971.

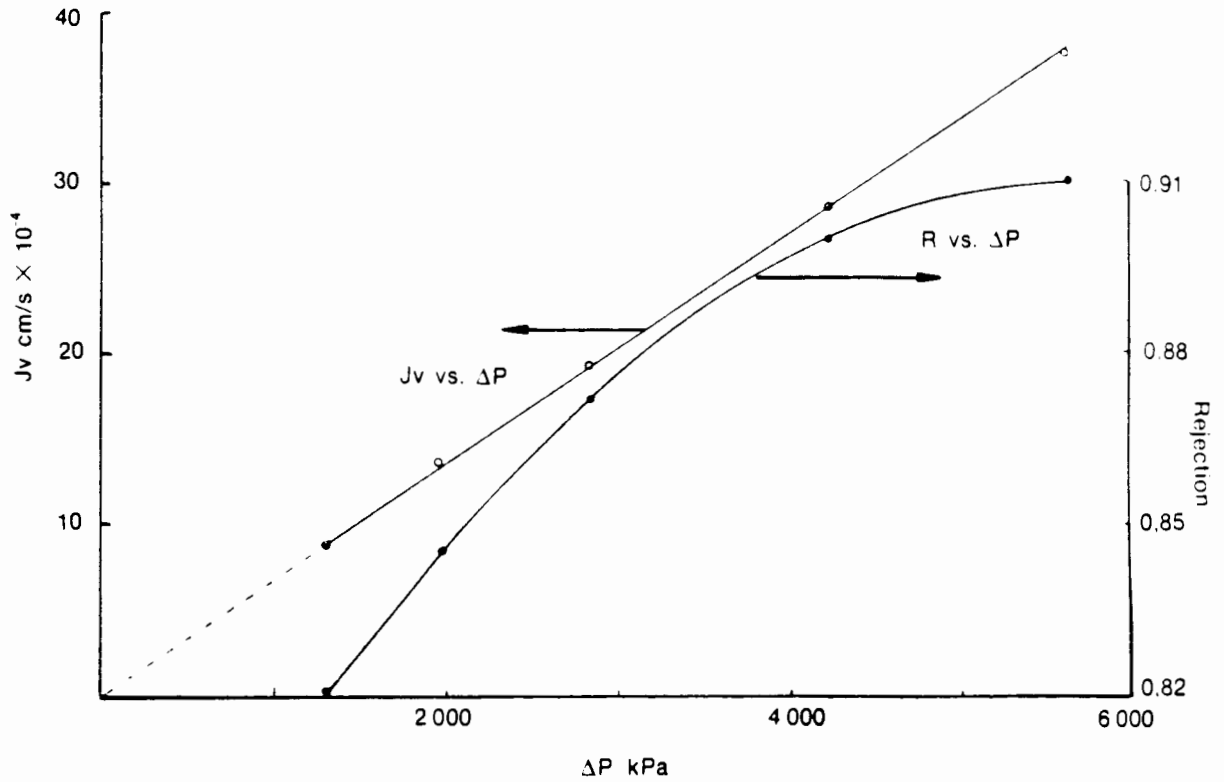


FIGURE 4.17: EFFECT OF OPERATING PRESSURE ON SOLVENT FLUX AND REJECTION; 1-PROPANOL; FT-30 MEMBRANE

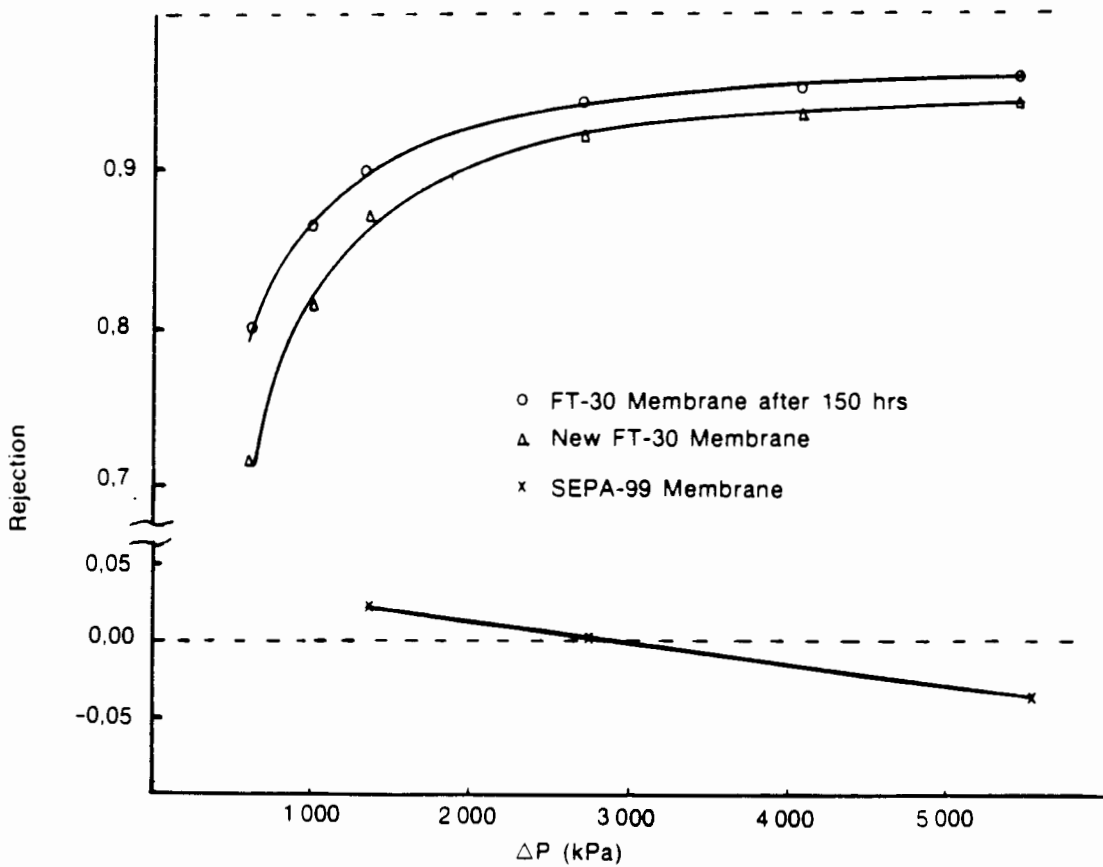


FIGURE 4.18: EFFECT OF OPERATING PRESSURE ON SOLVENT FLUX AND REJECTION; PHENOL

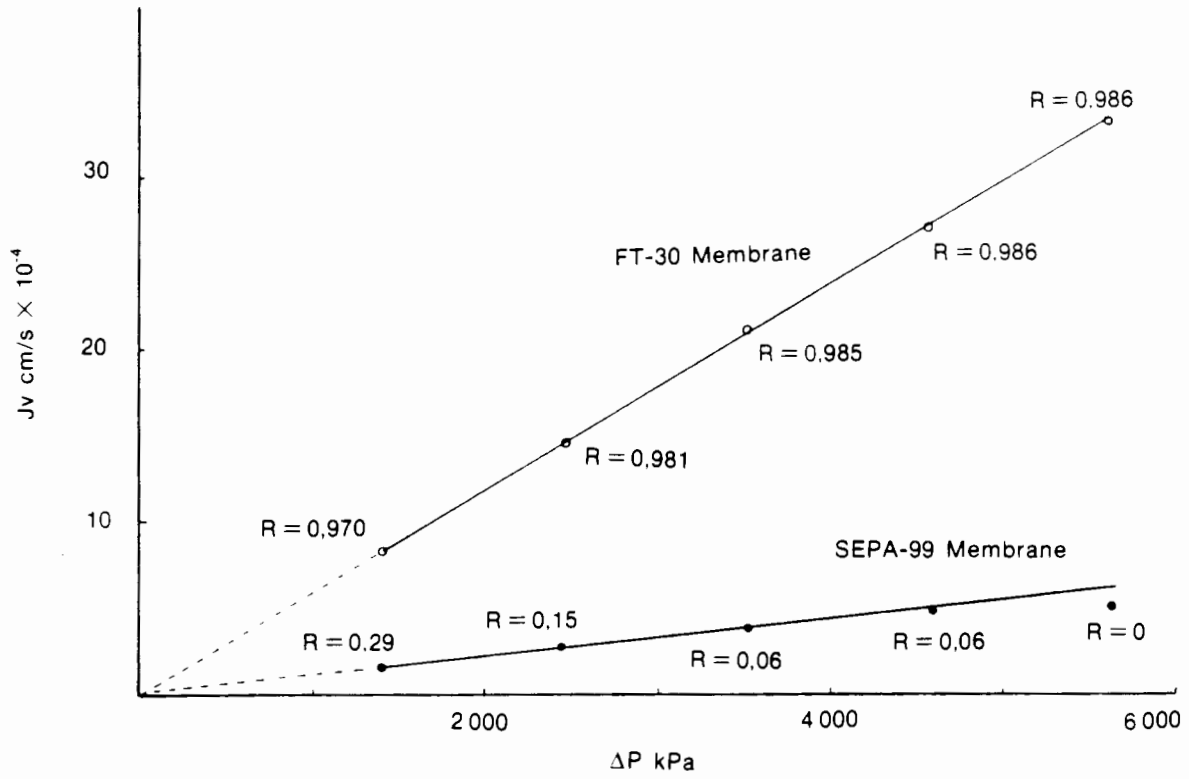


FIGURE 4.19: EFFECT OF OPERATING PRESSURE ON SOLVENT FLUX AND REJECTION; 4-n PROPYL PHENOL

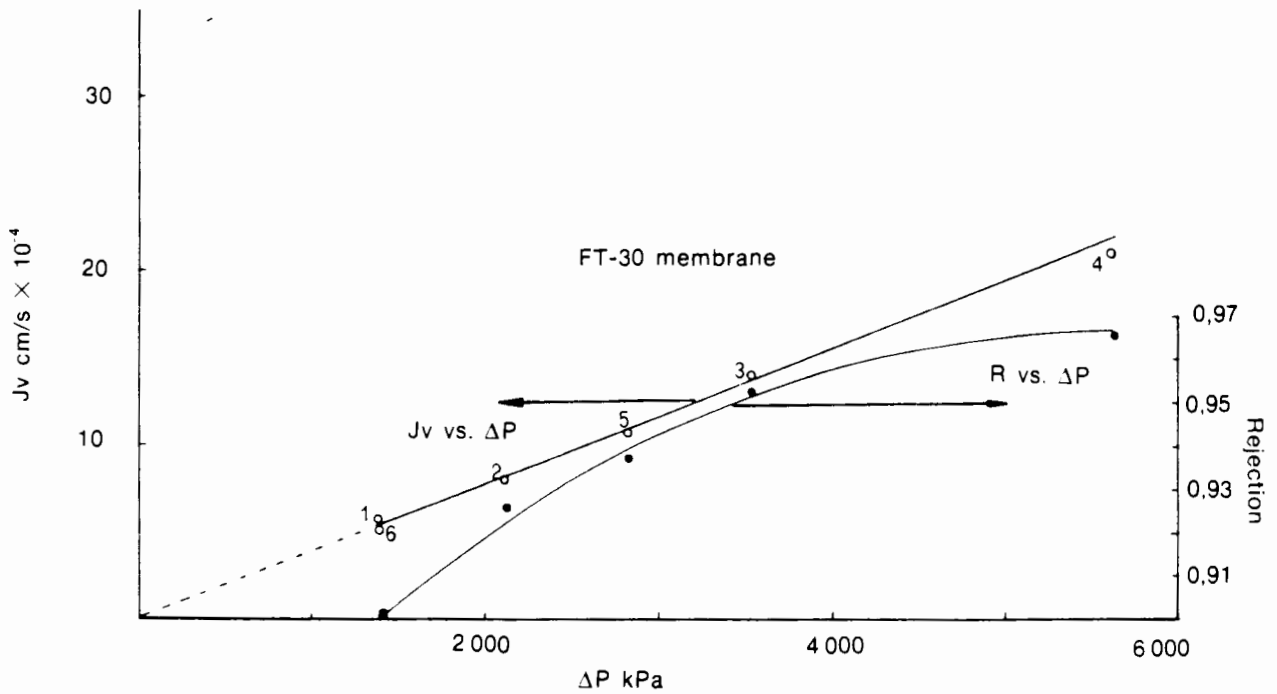


FIGURE 4.20: EFFECT OF OPERATING PRESSURE ON SOLVENT FLUX AND REJECTION; 4-METHYL PHENOL

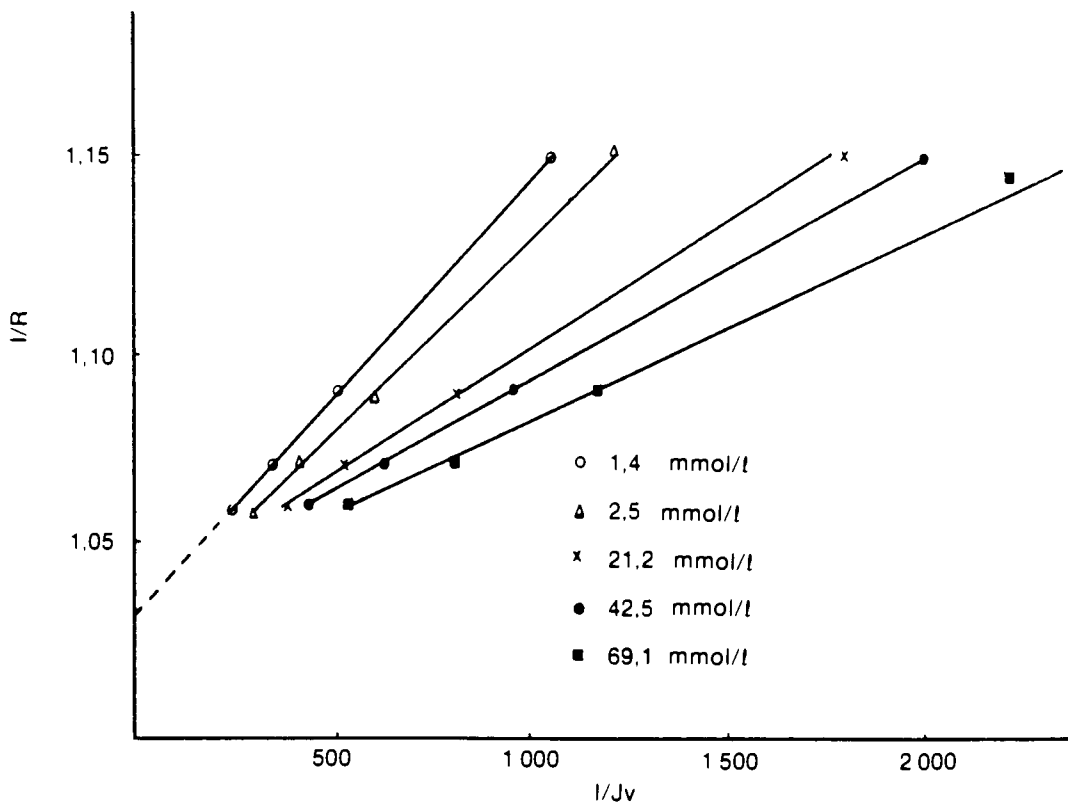


FIGURE 4.21: $1/J_v$ vs. $1/R$; PHENOL SOLUTIONS; FT-30 MEMBRANE

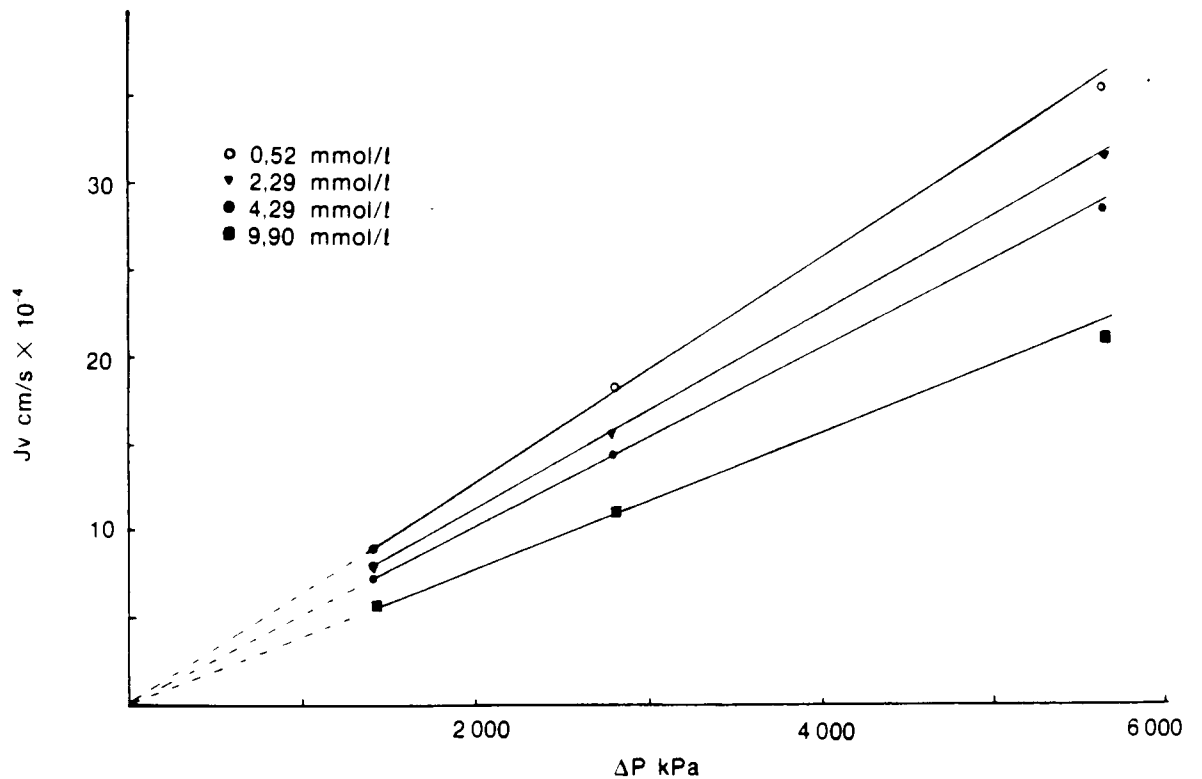


FIGURE 4.22: EFFECT OF FEED CONCENTRATION ON WATER FLUX; 1-HEPTANOL; FT-30 MEMBRANE

Cellulose acetate membranes do not follow this pattern especially with respect to the higher alcohols, such as 1-hexanol, and the phenols. This apparent anomaly may be a result of changes in the partitioning coefficient, K_s , of solute between solution and cellulose acetate membrane or changes in the diffusion coefficient, D_s , of solute in the membrane. Conceptually when solute is highly sorbed by the membrane a relatively large concentration driving force exists even with dilute feed solutions so that rejection of such a solute may be very poor. If the forces of sorption are relatively strong (the solute held strongly on the membrane surface for example) solute diffusion will be slow resulting in a good rejection. These effects are explored in detail in Sections 4.6.3 and 4.6.4.

4.6.2.2 Effect of feed concentration on water flux and solute rejection

The effect of feed concentration on water flux is accounted for by a reduction in effective pressure due to the osmotic pressure of the feed solution :

$$J_v = A(\Delta P - \Delta \pi)$$

With dilute feed solutions with low osmotic pressures J_v should be affected only to a very limited extent. However, Figure 4.22 and 4.23 for 1-heptanol and phenol, respectively show that there is indeed a marked reduction in flux at relatively low feed concentrations with low osmotic pressures. Furthermore, extrapolation of the values intercepts the x-axis at, or close to the origin. This would not have been the case if osmotic pressures were high. Extrapolations would have intercepted the axis at a value equal to the osmotic pressure. This phenomenon indicates that the hydraulic permeability of the membrane decreases at higher feed concentrations presumably as a result of solute sorbed by the membrane.

Only a limited degree of flux reduction at higher concentrations is observed for the lower alcohols and branched alcohols. 1-Hexanol and especially 1-heptanol as well as all the phenols exhibit relatively large flux reductions at higher concentration. This effect is discussed in Section 4.6.3 in terms of solute sorption by the membrane.

4.6.2.3 Effect of temperature on water flux and solute rejection

Figure 4.24 shows the effect of temperature on the rejection of phenol by the two membranes and on water flux. Flux increase for both membranes amounted to about 3% per 1°C over the range 25°C to 35°C although the absolute increase was very much higher for the FT-30 membrane. Rejection of phenol by the FT-30 membrane dropped from 0,925 in this particular case to 0,896 over the 10°C increase. Rejection by the cellulose acetate ranged from -0,2 to +0,1 at both temperatures so that no trend could be observed.

A change in temperature affects the hydraulic permeability constant A in

$$J_v = A (\Delta P - \Delta \pi)$$

as well as D_s (and probably K_s) in

$$J_s = \frac{K_s D_s}{\Delta \chi} (C_f - C_p)$$

Increasing temperature increases both permeate flux and solute flux. In desalination applications these increases are about equal so that rejection stays constant. However, the rejection of phenol by the FT-30 membrane dropped about 3% with a 10°C increase in feed temperature indicating a larger increase in D_s than in A .

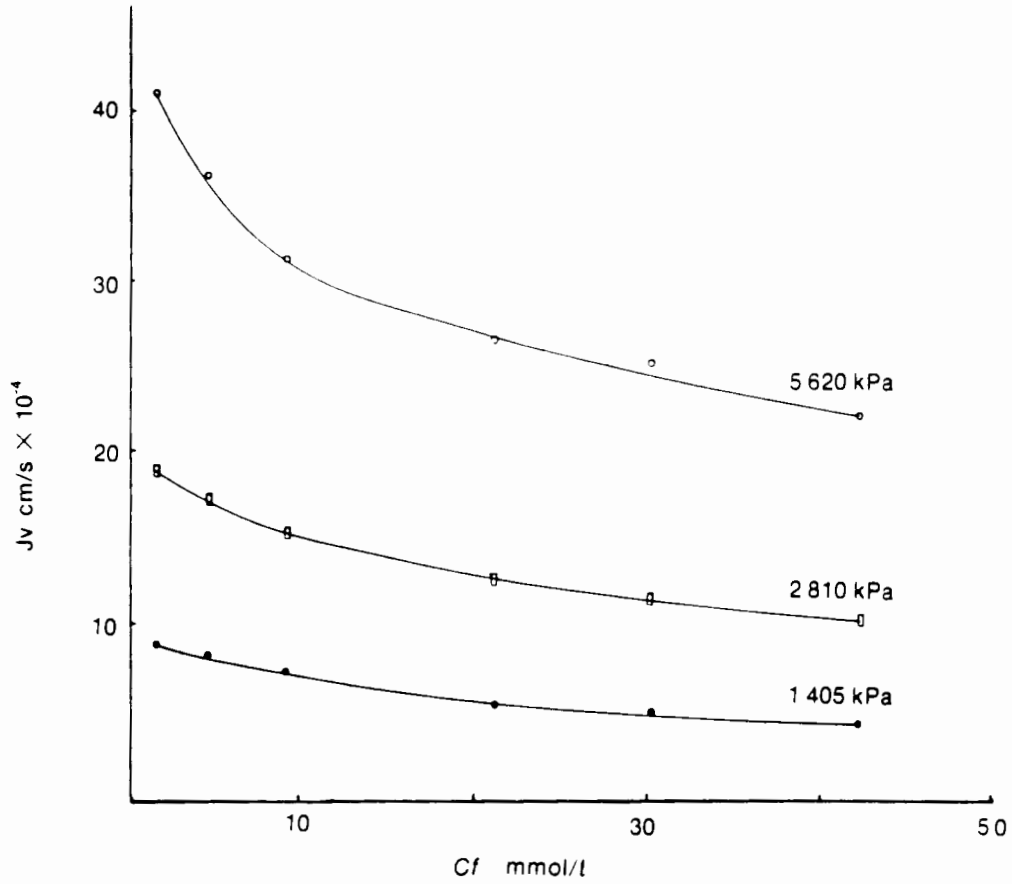


FIGURE 4.23: EFFECT OF FEED CONCENTRATION ON WATER FLUX; PHENOL; FT-30 MEMBRANE

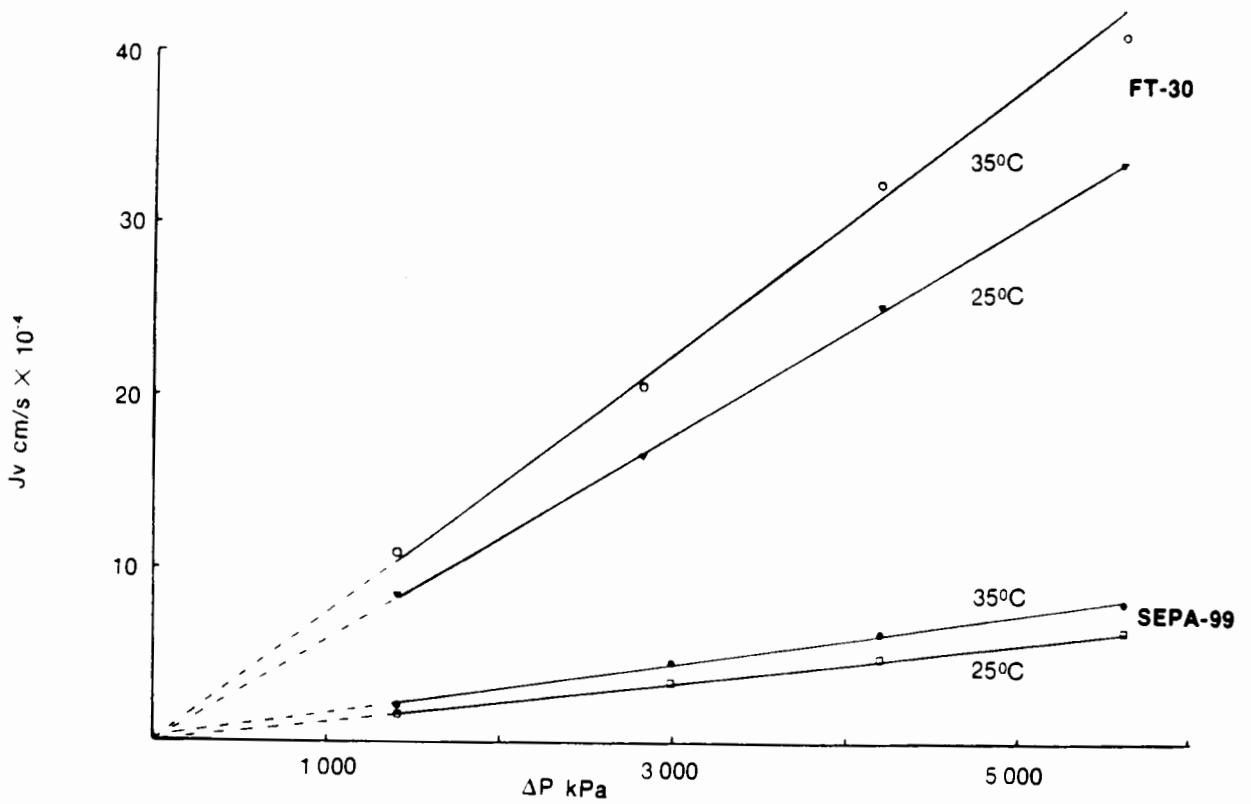


FIGURE 4.24: EFFECT OF TEMPERATURE ON WATER FLUX AND REJECTION; PHENOL

4.6.3 Sorption Data

The discussions in Section 4.6.2 indicate that solute flux through a membrane is largely determined by the degree of sorption of the solute by the membrane and the diffusion rate of solute in the membrane. Conceptually, differences in rejection of different solutes by the same membrane and of the same solute by different membranes should therefore be reflected by differences in sorption and diffusion rates. Using the procedures described in Section 4.4.3.2, an attempt was made to determine sorption by the different membranes of all the solutes under consideration. However, the amount of sorption of, especially the lower alcohols, was so small that it was not possible to determine any significant differences in the amounts sorbed by the membranes. Very accurate and reproducible determination of phenol in solution is possible and in view of the big difference in phenol rejection by the two membranes it was decided to focus the study on the sorption of phenol.

Sorption isotherms were determined using the procedures described in Section 4.4, and the data are given in Table 4.5 and Figures 4.25 - 4.28. Data from a series of tests using strips of rolled membrane in test tubes are summarized in Table 4.5. Since the composite membrane consists of three layers of material and since it is very difficult to separate the aromatic polyamide skin from the understructure, sorption by the polysulphone support membrane was also determined (PS in Table 4.5). The difference in sorption by the FT-30 membrane and the polysulphone membranes was ascribed to sorption by the polyamide skin. Table 4.5 shows that the bulk of phenol sorbed by the FT-30 membrane can be ascribed to sorption by the polysulphone. However, the amount sorbed per unit mass of material is higher for the polyamide than for the polysulphone which is again higher than for the cellulose acetate membrane.

TABLE 4.5:

**SORPTION DATA FOR FT-30, POLYSULPHONE AND SEPA-99 MEMBRANES
AND PHENOL SOLUTIONS**

Membrane	mmol/ 25 ml at To	mmol/ 25 ml at To + 2 hrs	mmol/ 25 ml at To + 5 hrs	mmol/ 25 ml at To + 24 hrs	mmol/ phenol sorbed	mmoles phenol sorbed per g of membrane material
FT-30	0.025	0.0083	0.0050	0.0028	0.0222	0.12*
PS	0.025	0.0092	0.0060	0.0037	0.0213	0.03
CA	0.025	0.0123	0.0097	0.0089	0.0161	0.02
FT-30	0.05	0.0216	0.0148	0.0068	0.0284	0.89
PS	0.05	0.0226	0.0171	0.0151	0.0349	0.05
CA	0.05	NA	NA	NA	NA	NA
FT-30	0.1	0.0620	0.0461	0.0226	0.0774	0.935
PS	0.1	0.0702	0.0528	0.0294	0.0706	0.10
CA	0.1	0.0741	0.0442	0.0357	0.0643	0.07
FT-30	0.175	NA	0.0727	0.0491	0.1259	1.09
PS	0.175	NA	0.0798	0.0570	0.118	0.17
CA	0.175	NA	NA	NA	NA	NA
FT-30	0.25	NA	NA	0.0829	0.1671	1.39
PS	0.25	NA	NA	0.0930	0.1570	0.23
CA	0.25	NA	NA	0.1047	0.1453	0.17

*Amount phenol adsorbed by aromatic polyamide was determined from the difference between the amount adsorbed by the FT-30 membrane and the polysulphone membrane and this difference was divided by the amount of polyamide in the strip of membrane.

Figure 4.25 shows the relative amounts of phenol sorbed as a function of concentration of the contact solution. This figure shows that the amount sorbed per unit mass increases with increasing concentration and that it levels off at higher concentrations. This may offer an explanation for the decrease in permeate flux with increasing feed concentrations, *viz.* that more phenol is sorbed at higher feed concentrations which will give a higher hydraulic resistance than at lower feed concentrations.

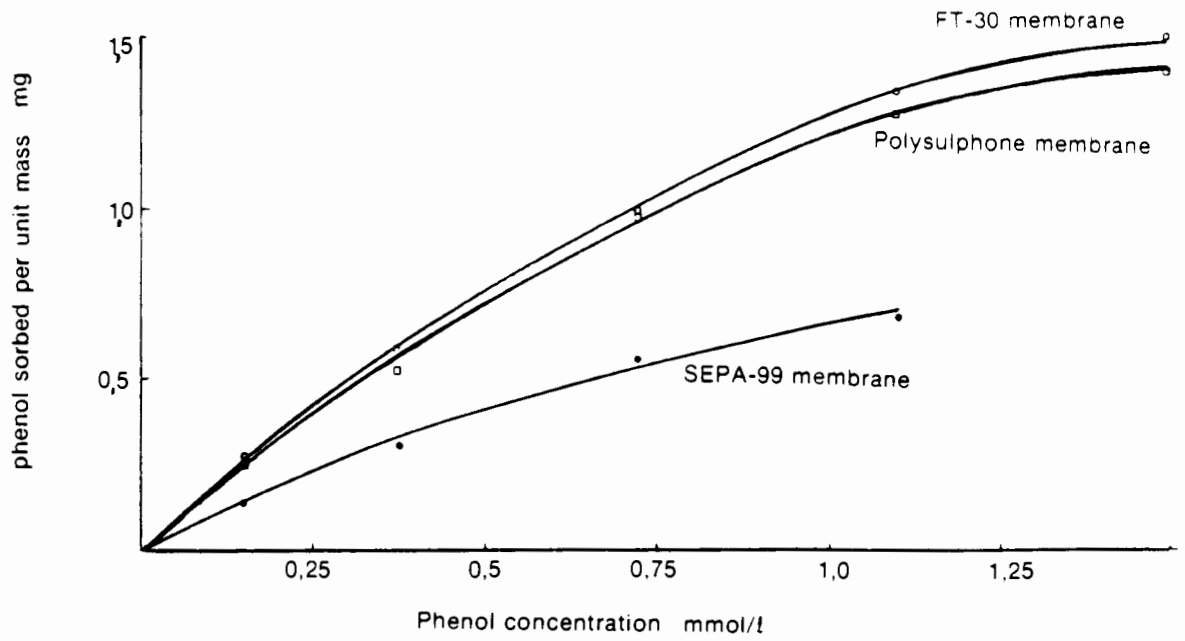


FIGURE 4.25 AMOUNT PHENOL SORBED vs. PHENOL CONCENTRATION IN SOLUTION

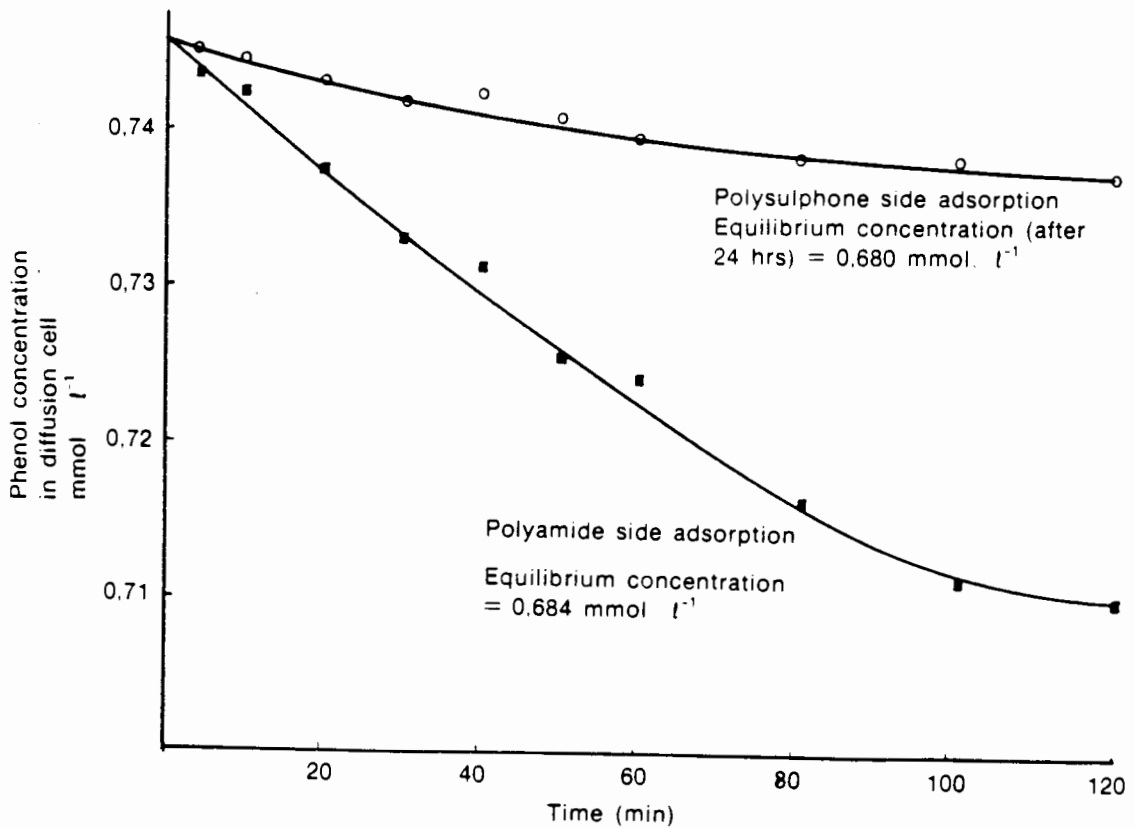


FIGURE 4.26: SORPTION FROM 0.745 mmole l⁻¹ PHENOL SOLUTION BY THE POLYAMIDE AND POLYSULPHONE SIDES OF FT-30 MEMBRANE

Figure 4.26 shows sorption data which were obtained in a different way. These sorption tests were conducted in the diffusion cell in order to differentiate between sorption by the polyamide skin and the polysulphone sides of the membrane. The change in concentration of the solutions (initially at the same concentration) in both compartments of the diffusion cell were measured at fixed intervals to determine the rates of sorption. This figure shows that sorption by the polyamide skin proceeds more rapidly than sorption by the polysulphone side, but that equilibrium concentrations are about the same. Desorption tests were also conducted in the diffusion cell. In this case the membrane was left for 24 hours in a phenol solution for sorption to be completed and equilibrium established. The membrane was then instantly rinsed in distilled water and placed in the diffusion cell. The two chambers of the diffusion cell were then filled with distilled water and the increase in phenol concentration measured at fixed intervals. Figure 4.27 shows data from such a test where the membrane was immersed in a 130 mmol/l phenol solution. Desorption proceeds much faster from the polyamide side than from the polysulphone side. These observations appear to be contradictory since a higher rate of sorption indicates stronger forces of attraction or sorption while faster desorption indicates weaker forces of attraction.

Similar results were obtained for the cellulose acetate membrane. Sorption and desorption also occurred at a higher rate from the skin side than from the porous support side. In this case the skin and support layers are from the same material, so that the phenomenon cannot be ascribed to different rates of sorption by the different materials (as may have been postulated for the FT-30 membrane).

The faster rates of both sorption and desorption from the skin sides of the membranes may be explained by the fact that sorption possibly takes place in the very finely porous membrane structure rather than on the membrane surface. This means that the denser skin will sorb

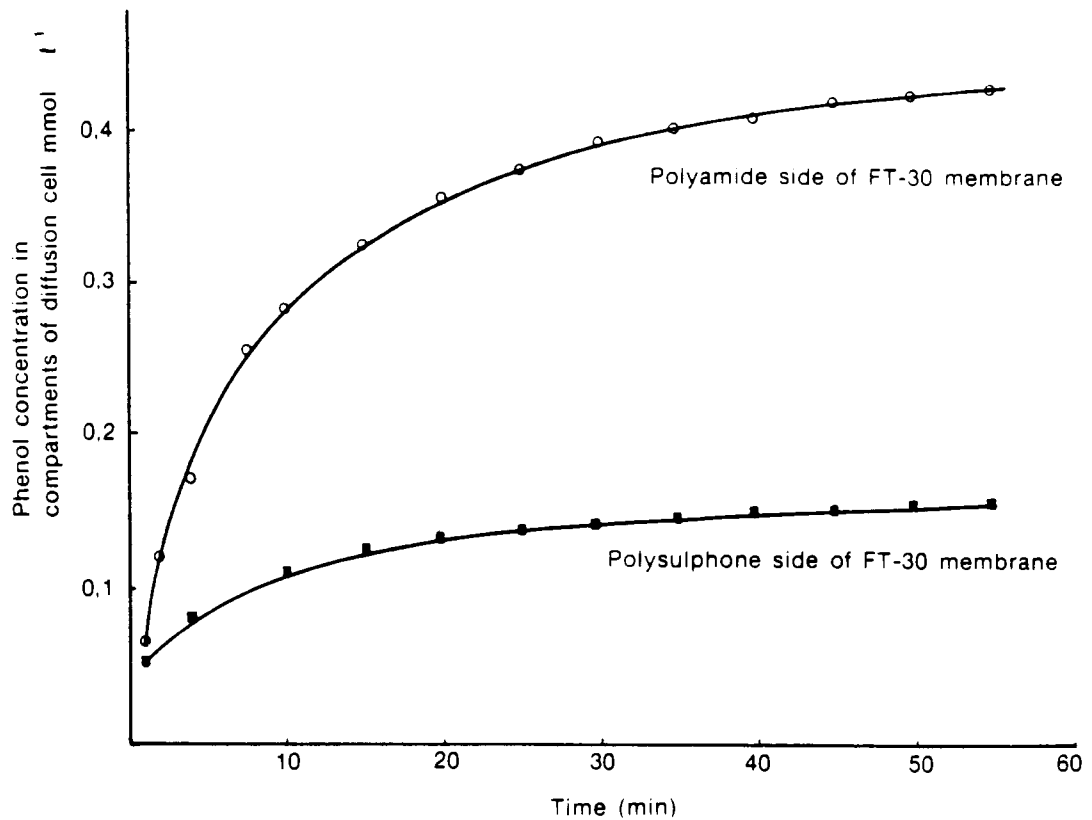


FIGURE 4.27: DESORPTION FROM A FT-30 MEMBRANE EQUILIBRATED IN 130 mmol l⁻¹ PHENOL

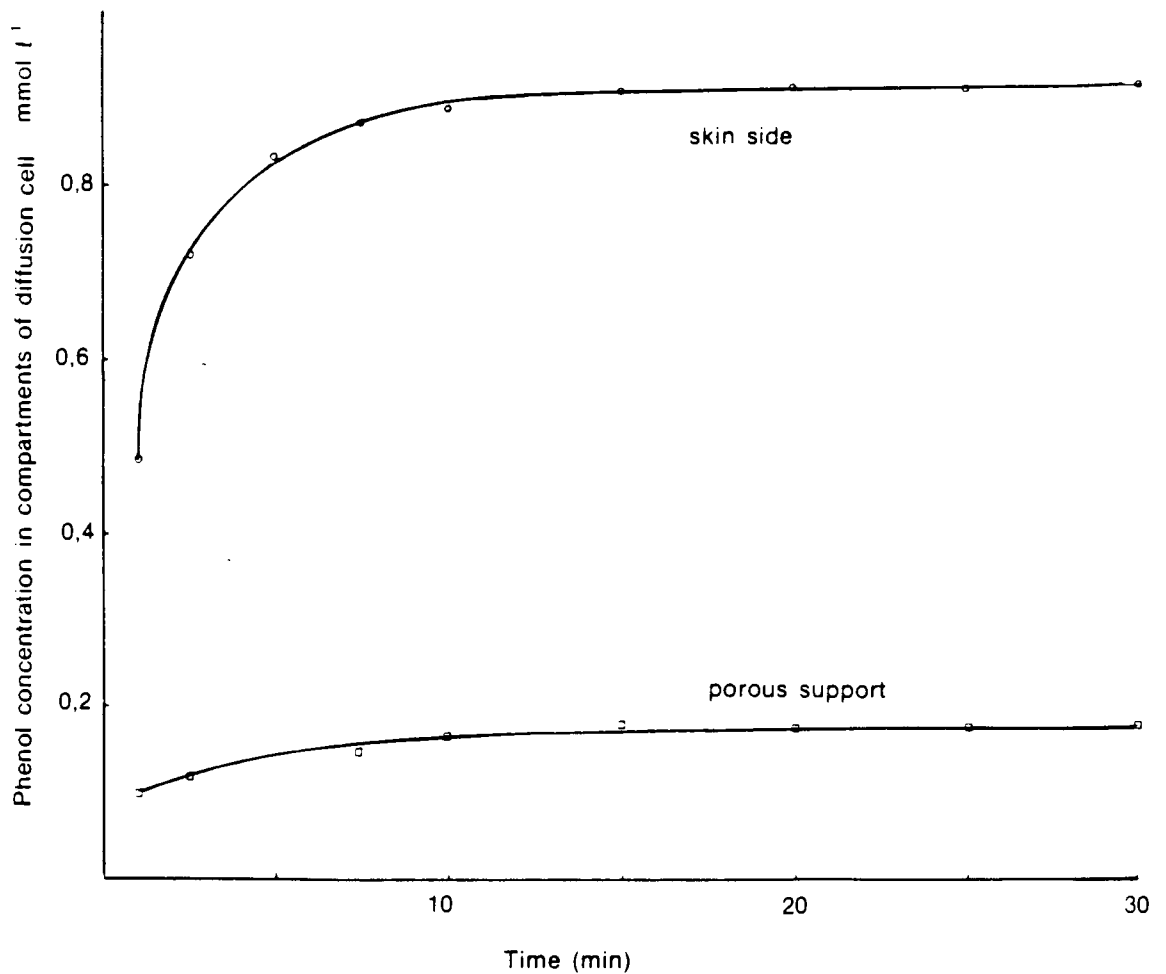


FIGURE 4.28: DESORPTION FROM CELLULOSE ACETATE MEMBRANE EQUILIBRATED IN 130 mmol/l PHENOL

more phenol per unit membrane area than the porous understructure giving a higher concentration gradient driving force from the skin side when the membrane is placed in pure water and therefore a faster rate of desorption. The same explanation also holds when the membrane is placed in a concentrated solution where the driving force for sorption is larger on the dense skin side than at the more porous understructure side because more sorption area is available in the denser skin side.

Figure 4.28 shows the rate of desorption from the cellulose acetate membrane under the same conditions as for the FT-30 membrane. It can be seen that the rate of desorption from the cellulose acetate membrane is very much higher than the desorption rate from the polyamide membrane indicating much stronger forces of attraction by the polyamide. These strong attractive forces indicate low diffusion rates in the FT-30 membrane and therefore good rejection. On the other hand the almost instantaneous desorption of phenol from the cellulose acetate membrane indicates relatively weak forces of attraction, high diffusion rates and poor rejection.

4.6.4 Diffusion Data

These tests were focussed on the diffusion of phenol in the FT-30, SEPA-99 and polysulphone membranes for the same reasons as discussed in Section 4.6.3. The procedures used in these tests are described in Section 4.4.3.3.

Concentrated phenol solutions were put in the skin side compartment of the diffusion cell and pure water in the other cell. The rate of change of phenol concentration in the clean water cell was then monitored until a constant rate was established. Figure 4.29 shows the rate of phenol permeation through the three membranes, while Figure 4.30 shows the rate of permeation through the FT-30 membrane on an extended scale. The phenol concentration at the start of the tests was 130 mmol/l.

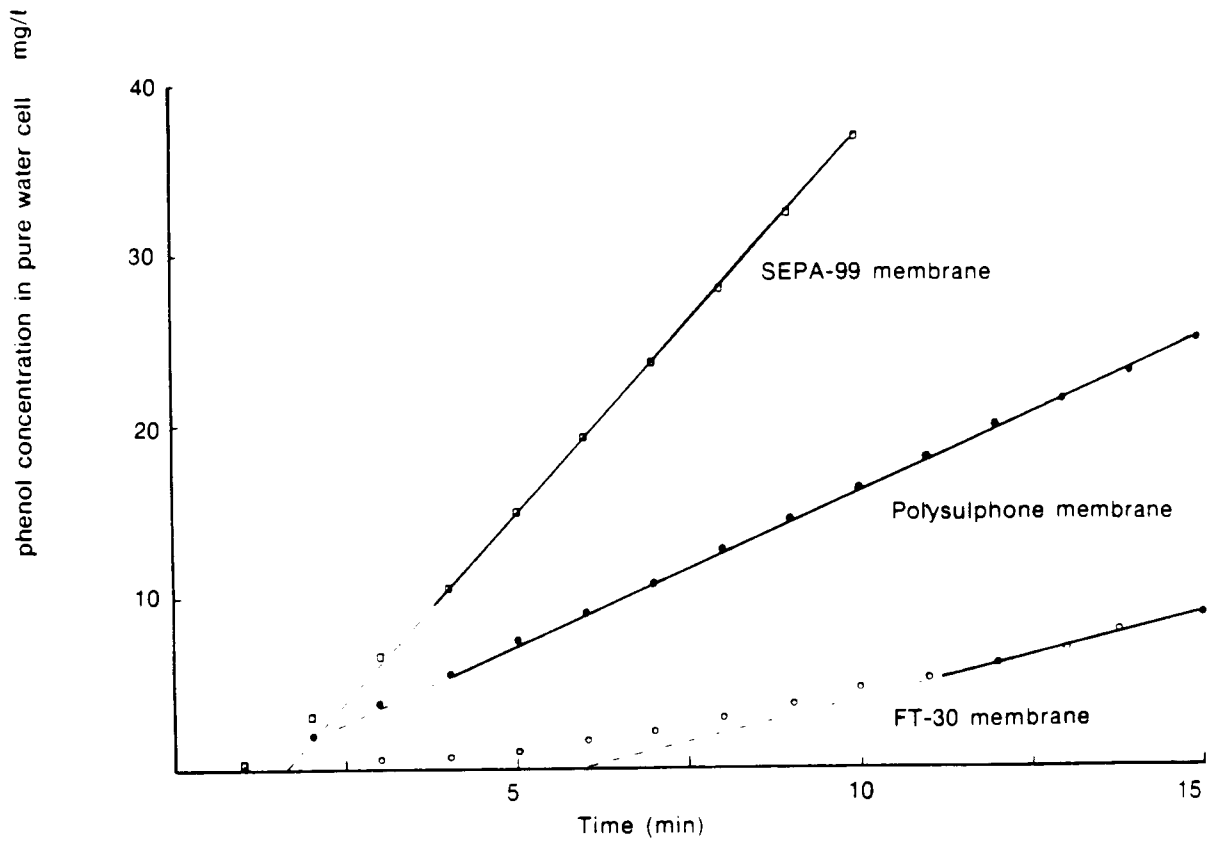


FIGURE 4.29: PHENOL PERMEATION vs TIME.

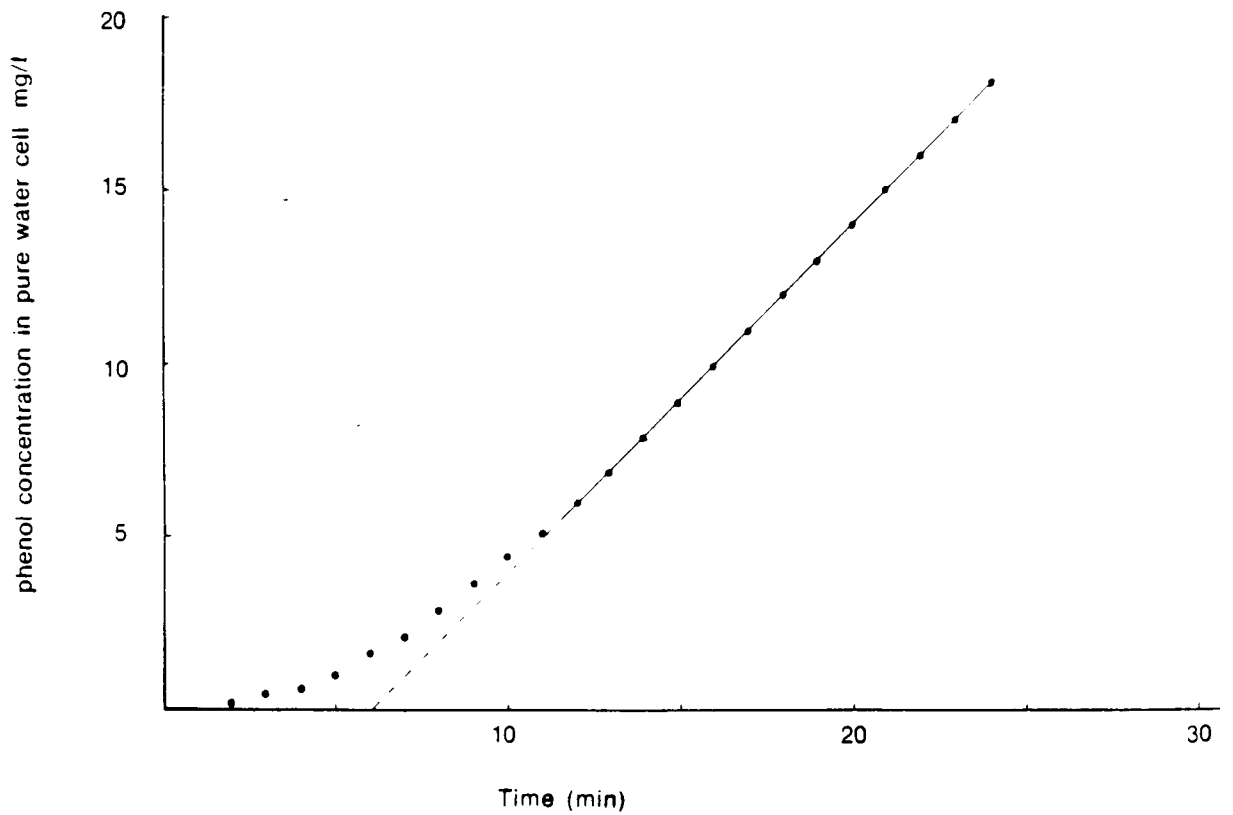


FIGURE 4.30: PHENOL PERMEATION vs TIME;
FT-30 MEMBRANE.

The rates of permeation through the membranes as calculated from the linear slopes of the plots in Figures 4.29 and 4.30 are

FT-30	: 7.3×10^{-7} mmol cm ⁻² sec ⁻¹
Polysulphone	: 17×10^{-7} mmol cm ⁻² sec ⁻¹
SEPA-99	: 37×10^{-7} mmol cm ⁻² sec ⁻¹

The very low permeation rate through the FT-30 membrane compared to the cellulose acetate SEPA-99 membrane is in line with phenol reverse osmosis data for these two membranes. However, the fact that the permeation rate through the polysulphone membrane is also lower than through the cellulose acetate membrane is unexpected in view of the more porous nature of the polysulphone membrane. This fact indicates that diffusive solute transport (at zero volume flux) depends to a greater extent on solute-membrane interaction than on porous structure.

These data confirm the observations from the desorption tests that phenol interacts more strongly with aromatic polyamide than with either polysulphone or cellulose acetate, resulting in higher phenol sorption by the polyamide, stronger forces of attraction and lower rates of diffusion.

A comparison of the sorption and desorption and permeation data for the cellulose acetate and polysulphone membranes indicates that the amount of phenol sorbed by polysulphone is higher than that sorbed by the cellulose acetate per unit membrane area and per unit membrane mass and that the rate of desorption from cellulose acetate is much higher than from polysulphone under similar conditions. These data point to relatively strong forces of attraction between polysulphone and phenol compared to cellulose acetate which may explain the higher rates of phenol permeation through the cellulose acetate membrane.

The rate of permeation through the polyamide skin of the FT-30 membrane was determined both directly and computed from the following :

$$\frac{1}{J_{SP} \text{ FT } 30} = \frac{1}{J_{SP} \text{ polyamide}} + \frac{1}{J_{SP} \text{ polysulphone}}$$

Using J_{SP} values for the FT-30 membrane and polysulphone membranes from Figure 4.33, gives

$$J_{SP} \text{ polyamide skin} = 12.8 \times 10^{-7} \text{ mmol cm}^{-2} \text{ sec}^{-1}$$

Measured permeation values ranged between 20 and $50 \times 10^{-7} \text{ mmol cm}^{-2} \text{ sec}^{-1}$.

The values given above are for the phenomenological process of permeation which does not necessarily represent diffusion in the membrane. In order to determine diffusion rates the actual concentration of solute in both surface layers of the membrane must be known. These values are not readily obtainable especially in laminated membranes such as the FT-30 membrane, but also in asymmetric membranes which can be considered as a very dense membrane on a porous support of the same material.

The permeation data discussed in this section confirm the observations from the desorption tests that phenol interacts more strongly with aromatic polyamide than with either polysulphone or cellulose acetate, resulting in larger phenol sorption by the polyamide, stronger forces of attraction, lower rates of diffusion and therefore good rejection of phenol by the FT-30 membrane compared to poor rejection by the cellulose acetate membrane.

4.7 EVALUATION OF MEMBRANE MODELS

4.7.1 Introduction

In order for a model to be truly predictive with respect to the rejection of different organic compounds, it should take into account the physical and chemical characteristics of the different solutes and solutions in order to differentiate between them. For this reason the models based on the thermodynamics of irreversible processes are not predictive in this sense. They do, however, allow analysis of reverse osmosis data, comparison of coefficients and prediction of changes in solute and solvent flux based on reverse osmosis data. The relationship between J_v and R which is discussed in Section 4.5.2.1 is an example of this type of analysis.

In this section the following models will be evaluated for use as simple predictive models :

- the solution-diffusion model,
- the preferential sorption-capillary flow model,
- correlations based on solubility parameters
- correlations based on the solvophobic theory.

4.7.2 Rejection and solute permeation

The permeation of solute through a membrane or rejection by a membrane may be expressed in a number of ways i.e.

$$(i) \quad \text{rejection of solute } R = \frac{C_f - C_p}{C_f}$$

$$(ii) \quad \text{solute flux } J_s \text{ mmol /cm}^2 \cdot \text{s} \approx J_v C_p$$

$$(iii) \quad \text{relative flux } \frac{J_s \bar{V}_s}{J_v \bar{V}_w} \approx \frac{J_v C_p}{J_v} \approx C_p$$

(concentration of solute in the product).

In comparing the transport of different solutes through a membrane these three expressions are linearly related, as long as the feed molar concentrations, C_f , and operating pressures are the same.

4.91

When comparing the transport of different solutes through a membrane the use of rejection does not give a complete picture of differences in transport behaviour. This may be illustrated by the hypothetical data in Table 4.6. These data show that when solute rejection is considered, membrane rejection R gives a good reflection of the situation. For example, if rejection drops from 0,95 to 0,90 the number of moles rejected drops proportionally i.e. from 9,5 to 9,0 in this example. However, when the number of moles permeating the membrane is of interest, rejection does not give a true reflection of the situation. In the example mentioned, when rejection drops from 0,95 to 0,90 (i.e. a 5% drop) there is a 100% increase in the number of moles permeating the membrane from 0,5 to 1,0 mol. Similarly when rejection drops from 0,995 to 0,95 (i.e. about 5%) there is a tenfold increase in the number of moles permeating the membrane.

Although these differences are only relative, they are important when considering the actual passage of molecules through a membrane and in attempting to relate changes in permeation to molecular characteristics. This is true especially when small differences in the high rejection range $>0,90$ are important. In such cases solute flux J_s offers a better means of comparison.

TABLE 4.6 REJECTION COMPARED TO PERMEATION

Rejection	Feed Conc, C_f mmol/l	Permeate conc, C_p mmol/l	mmol/l rejected	mmol/l permeated
0,50	10	5,0	5,0	5,0
0,80	10	2,0	8,0	2,0
0,90	10	1,0	9,0	1,0
0,95	10	0,5	9,5	0,5
0,990	10	0,10	9,90	0,10
0,995	10	0,05	9,95	0,05

4.7.3 Evaluation of the solution-diffusion model

The solution-diffusion model comprises the following equations :

$$J_v = A (\Delta P - \Delta \pi) \quad (4.46)$$

and $J_s = D_s K_s (C_f - C_p) / \Delta X \quad (4.49)$

where J_s is the solute flux

D_s is the solute diffusion coefficient

K_s is the partitioning coefficient of solute between membrane and solution.

The validity of this model for different solutes and membranes can be checked by plotting J_s vs $(C_f - C_p)$ according to Equation 4.49. The slope of this line is then $D_s K_s / \Delta X$, and if ΔX is known, values may be obtained for $D_s K_s$ for the different solutes which can then be compared with values of $D_s K_s$ determined experimentally. D_s values can be obtained from sorption or desorption tests as given by Crank and Park (1968).

$$\frac{C_t - C_\infty}{C_0 - C_\infty} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[- (2n+1)^2 \frac{\pi^2 D_s t}{\Delta X^2} \right] \quad \dots\dots\dots 4.117$$

Calculation of D_s from Equation 4.117 is very difficult but a good approximation may be obtained by simplifying this equation to

$$\frac{C_t - C_\infty}{C_0 - C_\infty} = \frac{8}{\pi^2} \exp \left[- \frac{\pi^2 D_s t}{\Delta X^2} \right]$$

for times longer than about one hour after the start of sorption or desorption tests.

Alternatively D_s values may be obtained from transient permeation tests according to the analysis by Paul (1979) of Fick's second law. Paul showed that when the transient flux, J_T is plotted against time the intercept of this line of the X-axis is given by

$$t = \theta = \frac{\Delta X^2}{6 D_s} \quad \dots\dots\dots 4.118$$

from which D_s may be calculated.

Figures 4.31, 4.32 and 4.30 show plots of J_s vs $C_f - C_p$, $\log \frac{C_t - C_\infty}{C_0 - C_\infty}$ vs t and J_t vs t respectively for phenol and the FT-30 membrane from which the following analyses can be made :

From Figure 4.31 :

The slope of this curve = $DsKs/\Delta\chi$

$$\begin{aligned} DsKs/\Delta\chi &= 2,1 \times 10^{-4} \text{ cm/s} \\ KsDs &= 2,1 \times 10^{-4} \times \Delta\chi \text{ cm}^2/\text{s} \\ &= (2,1 \times 10^{-4}) \times (3,52 \times 10^{-3}) \\ &= 7,4 \times 10^{-7} \text{ cm}^2/\text{s} \end{aligned}$$

From Figure 4.32 :

The slope of this curve = $\frac{-\pi^2 Ds}{\Delta\chi^2}$

$$\begin{aligned} Ds &= \frac{-\Delta\chi^2 (\text{slope})}{\pi^2} \\ &= \frac{(3,52 \times 10^{-3})^2 \times (-8,5 \times 10^{-5})}{\pi^2} \\ &= 1,07 \times 10^{-10} \text{ cm}^2/\text{s} \end{aligned}$$

From Figures 4.29 and 4.30 :

$$\begin{aligned} Ds &= \frac{(\Delta\chi)^2}{6\theta} \\ &= \frac{(3,5 \times 10^{-3})^2}{6 \times 6,4 \times 60} \\ &= 5,2 \times 10^{-9} \text{ cm}^2/\text{s} \text{ (FT-30 membrane)} \end{aligned}$$

For the polysulphone support membrane

$$Ds = 4,25 \times 10^{-8} \text{ cm}^2/\text{s}$$

For the polyamide skin of the FT-30 membrane

$$\begin{aligned} \frac{1}{D_s \text{ (FT-30)}} &= \frac{1}{D_{s(\text{PA})}} + \frac{1}{D_{s(\text{PS})}} \\ D_{s(\text{PA})} &= 5,9 \times 10^{-9} \end{aligned}$$

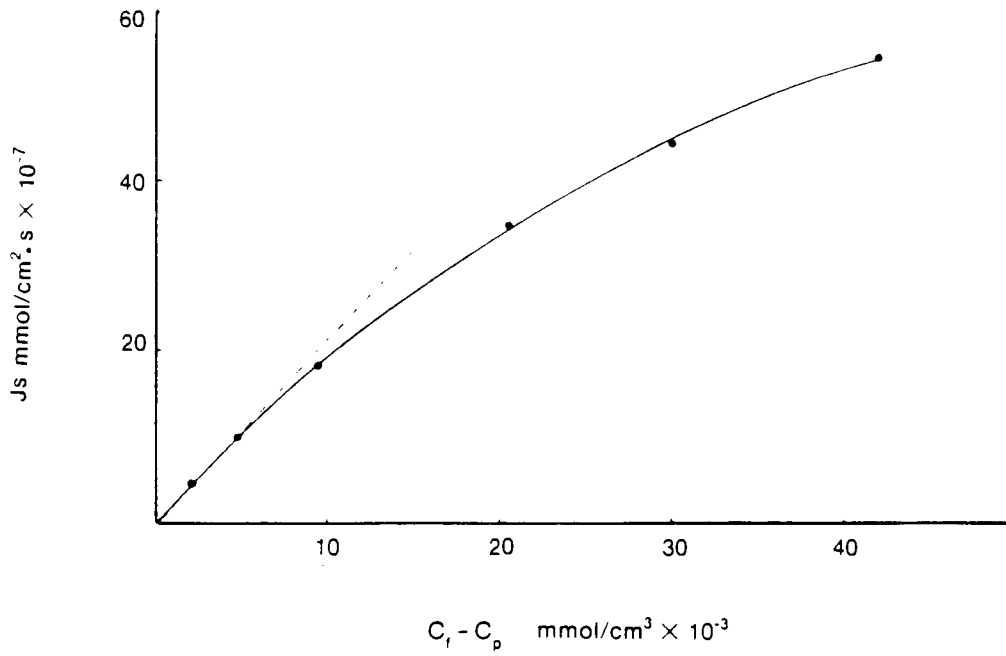


FIGURE 4.31: PHENOL FLUX AS A FUNCTION OF CONCENTRATION DRIVING FORCE; FT-30; 5 620 kPa

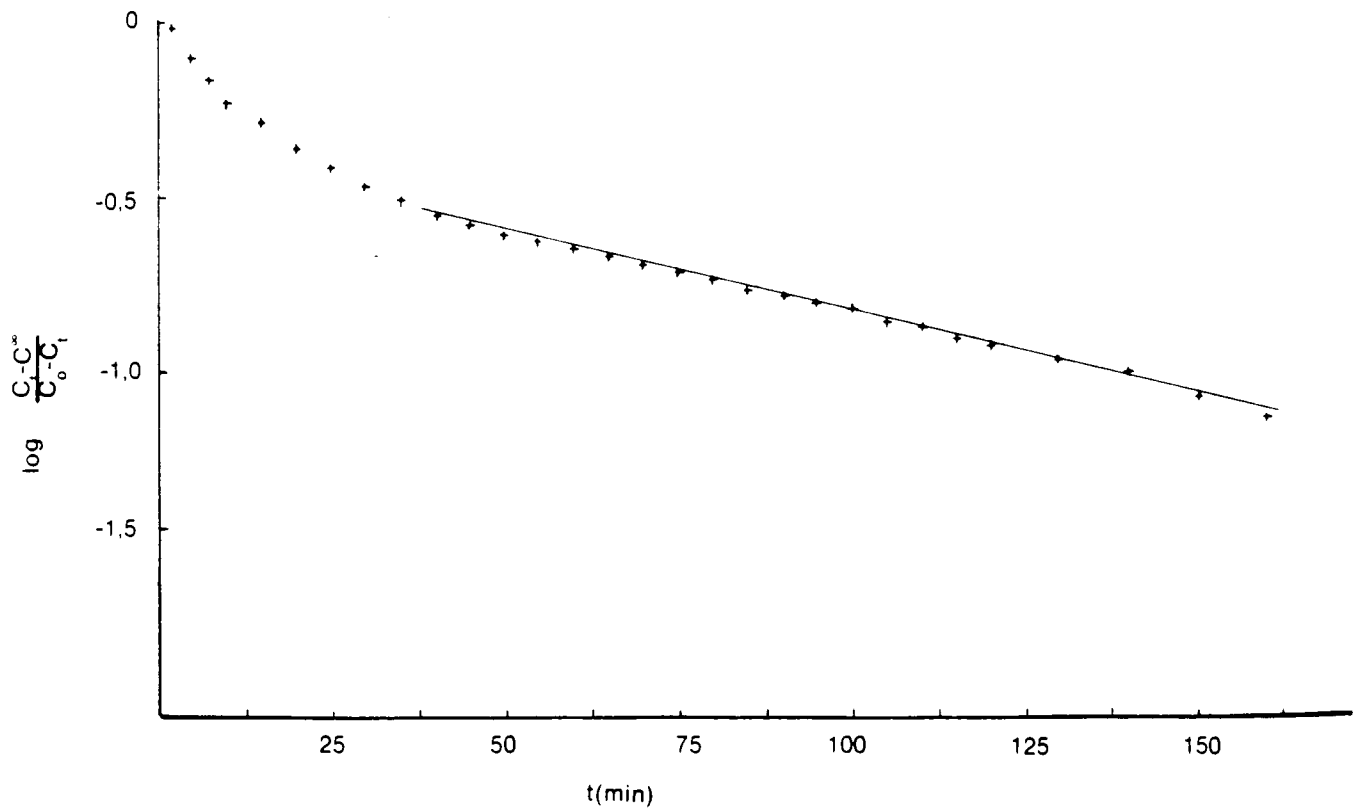


FIGURE 4.32: $\log \frac{C_i - C_i^\infty}{C_o - C_i}$ vs. t ; FT-30 MEMBRANE ; PHENOL

which shows that the diffusion coefficient for the whole membrane is determined by the coefficient of the very thin polyamide skin.

Values for the partitioning coefficient K_s were obtained from the data discussed in Section 4.6.3 as

$$K_s = \frac{\text{mass of solute per unit volume of membrane}}{\text{mass of solute per unit volume of solution}}$$

The values for K_s , D_s and $K_s D_s$ obtained by the different procedures are summarized in Table 4.7 for the FT-30 membrane and phenol.

TABLE 4.7 K_s , D_s and $K_s D_s$ EXPERIMENTAL VALUES FOR FT-30 MEMBRANE AND PHENOL

Source	D_s cm ² /s	K_s	$K_s D_s$ cm ² /s
Reverse osmosis data J_s vs $(C_f - C_p)$ (1)			$7,4 \times 10^{-7}$
Transient permeation (2)	$5,2 \times 10^{-9}$		
Elution from membrane (3)	$1,1 \times 10^{-10}$		
Partitioning (4)		$1,6 \times 10^3$	
(2)x(4) $D_s K_s$			$8,3 \times 10^{-6}$
(3)x(4) $D_s K_s$			$1,8 \times 10^{-7}$
(1)÷(2) K_s		$6,3 \times 10^2$	
(1)÷(3) K_s		3×10^3	
(1)÷(4) D_s	$2,1 \times 10^{-10}$		

The KsDs values from reverse osmosis data (1) and the values computed from laboratory analysis (2) x (4) and (3) x (4) differ by about one order of magnitude indicating a reasonably good correlation between the different experimental values.

Anderson et al (1972) and Jonsson (1980) reported Ks and Ds values for phenol and cellulose acetate membranes. Their values are given together with those obtained experimentally in this study in Table 4.8.

TABLE 4.8 Ks, Ds and KsDs EXPERIMENTAL AND LITERATURE VALUES FOR CELLULOSE ACETATE MEMBRANES AND PHENOL

Source	Ds cm ² /sec	Ks	KsDs cm ² /sec
Transient permeation (1)	$1,7 \times 10^{-8}$		
Partitioning (2)		$4,6 \times 10^2$	
(1) x (2)			$7,8 \times 10^{-6}$
Anderson <u>et al</u> (1972)	10×10^{-10}	$3,7 \times 10^1$	$3,7 \times 10^{-8}$
Jonsson (1980)	9×10^{-10}	3×10^1	$2,7 \times 10^{-8}$

In order for a model to be useful as a simple predictive model for the rejection of organic compounds, data for D_s and K_s should be readily obtainable from simple laboratory measurements or from the physical or chemical characteristics of the solutes. The wide variation in data and the discussion above indicate that this is not true for the solution-diffusion model. It is therefore concluded that this model is not suitable for the purpose of this study.

4.7.4 Evaluation of Preferential Sorption-Capillary Flow Model

This model which is described in Section 4.2.5 comprises of Equations 4.71 - 4.74. For dilute solutions where osmotic pressures are small Equation 4.77 may be used to calculate solute separation. Sourirajan and Matsuura (1978) used these equations and relationships to calculate rejection data for a large number of organic compounds by a cellulose acetate and by an aromatic polyamide-hydrazide copolymer membrane. The membranes are specified by the values in Table 4.9.

TABLE 4.9 MEMBRANE SPECIFICATIONS (SOURIRAJAN AND MATSUURA 1978)

Parameter	Cellulose Acetate	Aromatic Polyamide
A , g-mol H_2O/cm^2s atm	$1,660 \times 10^{-6}$	$1,300 \times 10^{-6}$
$(D_{sm}/K\delta)_{NaCl}$ cm/s	$1,790 \times 10^{-5}$	$1,470 \times 10^{-5}$
X_{s2}	—	$1,386 \times 10^{-3}$

The calculated rejection data are given in Table 4.10 together with data from this study.

TABLE 4.10 CALCULATED AND EXPERIMENTAL REJECTION DATA
(SOURIRAJAN AND MATSUURA 1978)

Solute	Cellulose Acetate		Aromatic Polyamide	
	S & M 2847 kPa	This study 2810 kPa	S & M 2847 kPa	This study 2810 kPa
NaCl	0,968	0,979	0,984	0,993
Methanol	0,094		0,253	0,28
Ethanol	0,182	0,24	0,700	0,65
1-propanol	0,293		0,802	0,86
2-propanol	0,480		0,870	0,95
1-butanol	0,218	0,17	0,839	0,92
2-butanol	0,497		0,915	0,97
2 methyl-1 propanol	0,497		0,869	0,975
2 methyl-2 propanol	0,868	0,80	0,987	0,990
1-pentanol	0,185		0,894	0,92
1-hexanol	0,155	0,09	0,947	0,94
1-heptanol	0,131		0,926	0,96
Acetone	0,278	0,24	0,646	0,71
2-butanone				0,77
3-pentanone	0,317	0,37	0,784	0,78
Cyclopentanone	0,533			
Cyclohexanone			0,953	0,97

It is evident from Table 4.10 that there is a reasonably good agreement between the experimental rejections from this study and the calculated values from the Sourirajan-Matsuura model. However, this model does not hold for solutes and membranes where the solute is preferentially sorbed. The phenols fall in this category and some higher alcohols and their rejection can therefore not be calculated by this procedure. This model does, therefore, not comply with the requirements of this study. It is, furthermore, quite a complicated procedure to determine and calculate the various membrane parameters and coefficients required for the set of equations to calculate the rejection of a particular solute by a membrane.

4.7.5 Correlations based on solubility parameters

The concept of using solubility parameters for the partitioning of solute between membrane and solution was introduced in Section 4.2.4.2. The total solubility parameter δ_T may be used for this purpose or, alternatively the three components, δ_p , δ_d and δ_h may be used to represent the polar, dispersion and hydrogen bonding interactions between solute and membrane.

Spencer and Gaddis (1979) analysed the dependence of rejection on solubility parameters. They assumed that the concentration of solute available for transport across the membrane depends on the difference in solubility parameters characterizing the membrane and solute respectively.

$$\Delta_{sm} = \delta_s - \delta_m$$

They determined the δ_m value of a particular membrane as the δ value at $R = 0$ when plotting rejection versus solubility parameters for a particular membrane and concluded that for systems with $-10 \times 10^3 < \Delta_{sm} < 0 \text{ (J/m}^3\text{)}^{\frac{1}{2}}$ the rejection of solute should be higher than about 90% for membranes other than cellulose acetate.

Table 4.11 and Figure 4.33 shows rejection and solubility parameter values (where available) for the membranes and solutes used in this study. It is evident from these data that there is indeed a fairly good correlation between the total solubility parameter and the rejection of solutes by the FT-30 membrane. The correlation coefficient of Figure 4.33, $r = 0,8342$. These data are plotted in Figure 4.34 in terms of $\ln J_s$ vs solubility parameter, and in this case the correlation coefficient, $r = 0,6611$

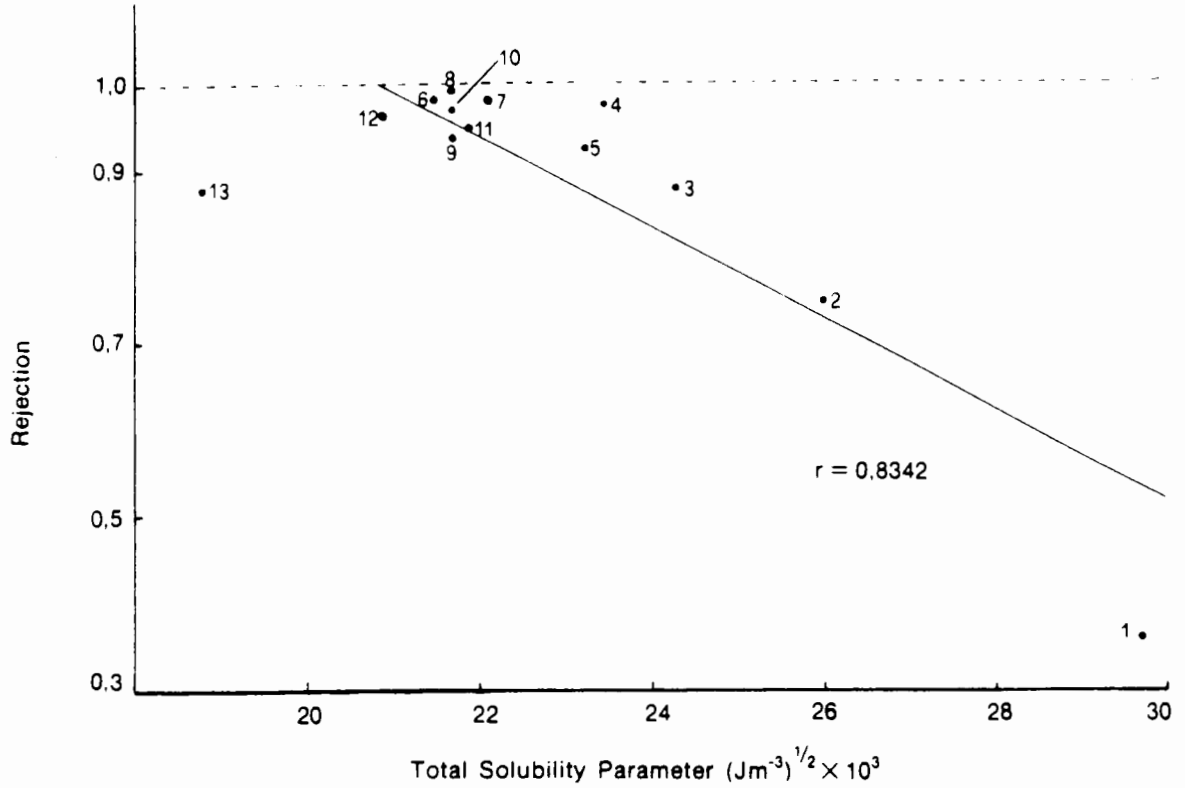


FIGURE 4.33: REJECTION vs. TOTAL SOLUBILITY PARAMETER; FT-30 (SOLUTE NUMBERS IN TABLE 4.11)

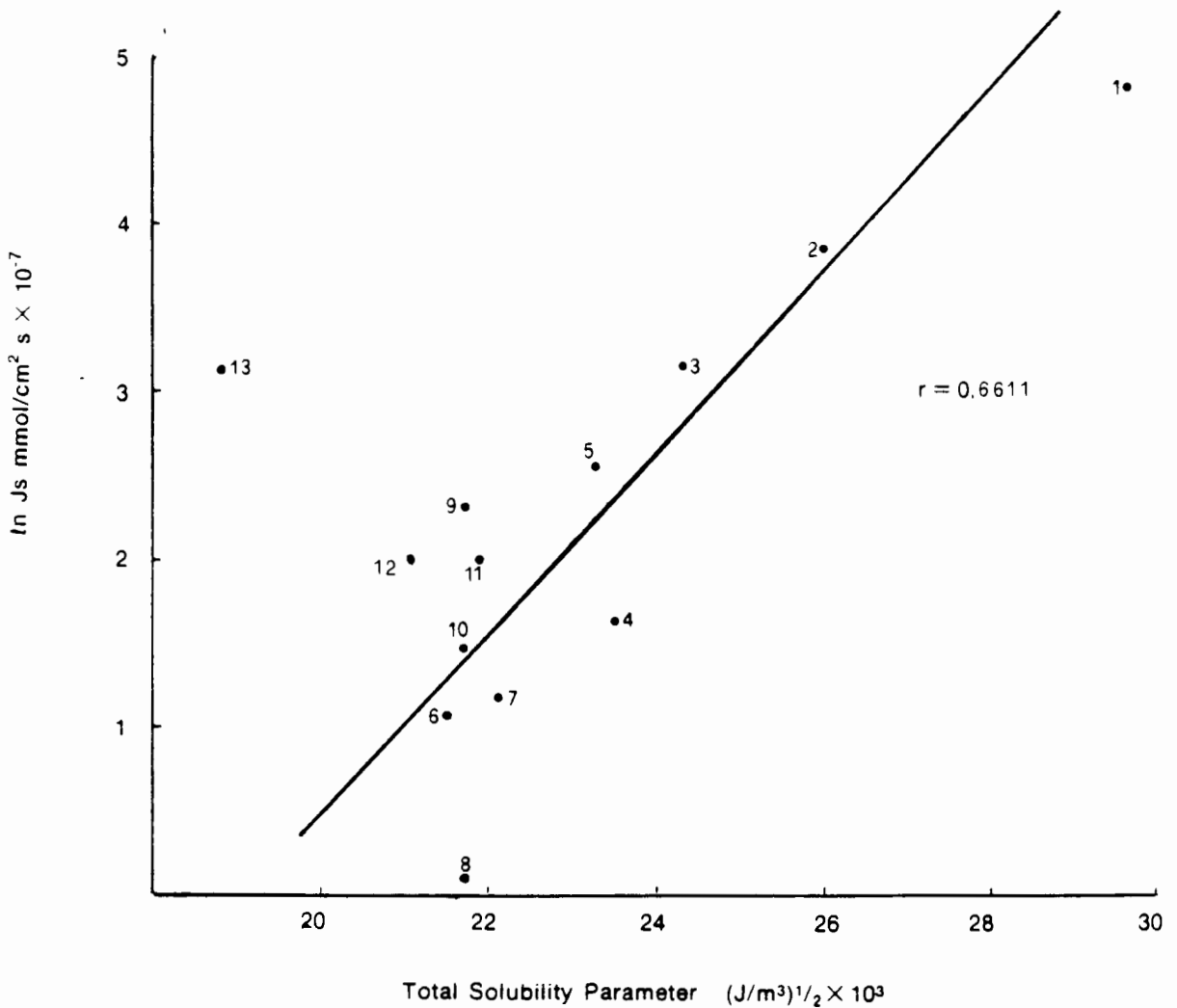


FIGURE 4.34: SOLUTE FLUX vs. TOTAL SOLUBILITY PARAMETER FT-30 (SOLUTE NUMBER IN TABLE 4.11)

TABLE 4.11 REJECTION AND SOLUBILITY PARAMETER VALUES

Solute (Number)	R:FT-30	R:SEPA-99	δ_T	δ_P	δ_d	δ_h
			J/m ³ x10 ⁻³			
Methanol (1)	0,36	0,27	29,7	12,3	15,2	22,3
ethanol (2)	0,75		26,0	8,8	15,8	19,5
1-propanol (3)	0,88		24,3	6,8	15,9	17,4
2-propanol (4)	0,976	0,23	23,5	5,7	16,0	15,8
1-butanol (5)	0,93		23,3			
2-butanol (6)	0,982		21,5			
2-methyl- 1-propanol (7)	0,984		22,1			
2-methyl- 2-propanol (8)	0,994	0,84	21,7			
1-pentanol (9)	0,944	0,07	21,7	4,5	16,0	13,9
1-hexanol (10)	0,955		21,9			
1-heptanol (11)	0,967		21,7	5,1	18,1	12,9
4 methyl phenol(12)	0,967		20,9			
benzene (13)	0,88		18,8			
water (14)			47,9	31,3	12,3	34,2

It should be noted that this model does not include a transport parameter. The correlation is based entirely on the chemical characteristics of the different solutes without taking differences in the rate of diffusion into account.

It is concluded that this model gives a reasonable indication of the rejection by the FT-30 membrane of the alcohols tested. However, since only one solubility parameter is available for the phenols no conclusion can be drawn with respect to a correlation between rejection and solubility parameters for the phenols.

4.7.6 Evaluation of the Solvophobic Theory as a Predictive Model for the Rejection of Organic Compounds

The application of the solvophobic theory to reverse osmosis rejection of organic compounds was introduced in Section 4.3. It was shown that the total cavity surface area (TSA) can be used to universally describe the nett free energy change in an association reaction, $\Delta G_{\text{net}}/RT$ since both the free energy change for cavity formation, ΔG_{cav} and the dominant counteracting dispersion force ΔG_{vdw} are linearly related to TSA. The total cavity surface area should therefore give a quantitative indication of the sorption (or partitioning) of organic solutes by a membrane. It is also shown that differences in the diffusion coefficient of solutes are reflected by differences in the size and hydrodynamic shape of the molecule and by forces of interaction between the diffusing molecule and the membrane. The forces of interaction as well as the size of the molecule are accounted for by the solvophobic theory. It is, therefore, only necessary to incorporate a factor to account for the shape of the molecule. A factor based on the ratio of cross-sectional areas of molecules was introduced for this purpose, so that

$$\ln J_s = \phi + \zeta \sqrt{A_{xs}} / A_{xn} \text{ (TSA)} \quad \dots\dots\dots 4.114$$

For simple aliphatic molecules A_{xn} is taken as the cross-sectional area of a linear molecule and assigned a value of 1, while A_{xs} is given a value of 2 for single-branched molecules, and 3 for double-branched molecules. For aromatic molecules, benzene is similarly taken as reference with a value of 1.

Total cavity surface areas are calculated from geometrical considerations. The X, Y, and Z coordinates of the solute atoms are determined from known bond lengths and angles. TSA is then calculated using computer optimized surface areas from an energy minimization of the molecular configuration (Woodfield 1982). These values are given in Table 4.12 together with the factor for hydrodynamic shape.

TABLE 4.12. SOLUTE CAVITY SURFACE AREAS

Solute	Mol. mass	Cavity surface area TSA nm ² x 10 ⁻²	Factor for hydrodynamic shape	Adjusted TSA
Aliphatic compounds				
METHANOL	32,0	159,4	1	159
ETHANOL	46,1	190,1	1	190
1-PROPANOL	60,1	220,8	1	221
2-PROPANOL	60,1	215,9	1,4	302
1-BUTANOL	74,1	251,5	1	252
2-BUTANOL	74,1	243,9	1,4	340
2-METHYL 1-PROPANOL	74,1	242,3	1,4	339
2-METHYL 2-PROPANOL	74,1	238,9	1,75	418
1-PENTANOL	88,2	282,2	1	282
1-HEXANOL	102,2	312,9	1	313
1-HEPTANOL	116,2	343,6	1	344
Aromatic Compounds				
PHENOL	94,1	249	1	249
4-METHYL PHENOL	108,1	274	1	274
4-ETHYL PHENOL	122,1	306	1	306
2,6-DIMETHYL PHENOL	122,1	266	1,4	372
4-n-PROPYL PHENOL	136,2	337	1	337
4-ISOPROPYL PHENOL	136,2	322	1,22	393
BENZENE	78,1	207	1	207
TOLUENE	92,2	232	1	232

Table 4.13 gives the solute and solvent flux values for dilute alcohol solutions and the FT-30 membrane, together with adjusted TSA values and the molecular mass, while Table 4.14 gives the same data for the alkyl phenols. Solute flux versus adjusted TSA data are plotted in Figures 4.35 and 4.36 for alcohols and phenols respectively.

The regression line shown in Figure 4.35 has an excellent correlation coefficient r -value of 0,9841 while the r -value of the regression line in Figure 4.36 at 0,9536 for the phenols is also very good. These values confirm that the transport (and rejection) of a series of alkyl alcohols and of an aromatic series of alkyl phenols correlates extremely well with the adjusted total cavity surface area of the solvophobic theory. The solvophobic theory as adapted to the transport of organic solutes in reverse osmosis membranes, therefore, provides a good and simple predictive means for the rejection of alkyl alcohols and alkyl phenols by the composite FT-30 membrane.

Total cavity surface areas are, however, not readily available in the literature and it is therefore desirable to simplify this model even further. A possible simplification may be introduced by noting that molecular mass is linearly related to total surface area for the linear alcohols but this obviously does not hold for branched isomers. It is, however, also true that the differences in total surface area between branched isomers are relatively small, viz only about 5% for 1-butanol and its isomers so that it is reasonable to expect that the factor introduced earlier to account for differences in hydrodynamic shape will sufficiently compensate for these differences. This postulate is tested in Figures 4.37 and 4.38 where $\ln J_s$ is plotted against molecular mass adjusted by the factor for hydrodynamic shape. The regression line in Figure 4.37 has a correlation coefficient r -value of 0,9595 for the alkyl alcohols while the regression line for the phenols has an r -value of 0,9403 (Figure 4.38). These correlation coefficients are significantly

TABLE 4.13. SOLUTE AND SOLVENT FLUX THROUGH FT-30 MEMBRANE AT 5620 kPa AND 5 mmol/l FEED SOLUTION, CORRECTED TSA, MOL MASS

Solute (Number)	C_p (mmol/cm ³ $\times 10^{-4}$)	J_v at 5620 kPa (cm/s $\times 10^{-4}$)	J_s at 5620 kPa (mmol/cm ² .s $\times 10^{-7}$)	$\ln(J_s \times 10^{-7})$	Adjusted TSA (nm ² $\times 10^{-2}$)	Mol. mass
METHANOL (1)	32,1	38,0	122	4,80	159	32,0
ETHANOL (2)	12,5	36,6	46	3,83	190	46,1
1-PROPANOL (3)	6,0	38,1	23	3,14	221	60,1
2-PROPANOL (4)	1,3	38,1	5	1,61	302	60,1
1-BUTANOL (5)	3,5	37,1	13,0	2,56	252	74,1
2-BUTANOL (6)	0,9	36,1	3,3	1,19	341	74,1
2-METHYL 1-PROPANOL (7)	0,81	36,0	2,9	1,06	339	74,1
2-METHYL 2-PROPANOL (8)	0,3	36,2	1,1	0,095	418	74,1
1-PENTANOL (9)	2,8	36,1	10,1	2,31	282	88,2
1-HEXANOL (10)	2,3	32,0	7,4	2,00	313	102,2
1-HEPTANOL (11)	1,6	26,9	4,3	1,46	344	116,2

TABLE 4.14. SOLUTE AND SOLVENT FLUX THROUGH FT-30 MEMBRANE AT 5620 kPa AND 2 mmol/l PHENOL FEED SOLUTION

Solute	Cp mmol/cm ³ x 10 ⁻⁵	Jv at 5620 kPa cm/sx10 ⁻⁴	Js at 5620 kPa mmol/cm ² .s x10 ⁻⁸	ln(Js x 10 ⁻⁸)	Corrected cavity surface area nm ² x 10 ⁻²	mol mass
PHENOL 1	12	34,0	40,8	3,71	249	94,1
4-METHYL PHENOL 2	6,6	32,1	21,2	3,05	274	108,1
4-ETHYL PHENOL 3	6,0	31,4	18,8	2,93	306	122,1
4-n PROPYL PHENOL 4	4,0	30,0	12,0	2,48	337	136,2
4-ISOPROPYL PHENOL 5	2,4	30,4	7,3	1,99	451	136,2
2,6-DIMETHYL PHENOL 6	1,8	29,7	5,3	1,67	466	122,1
BENZENE 7	24	39,5	94,8	4,56	207	78,1
TOLUENE 8	13	38,6	50,2	3,92	232	92,1

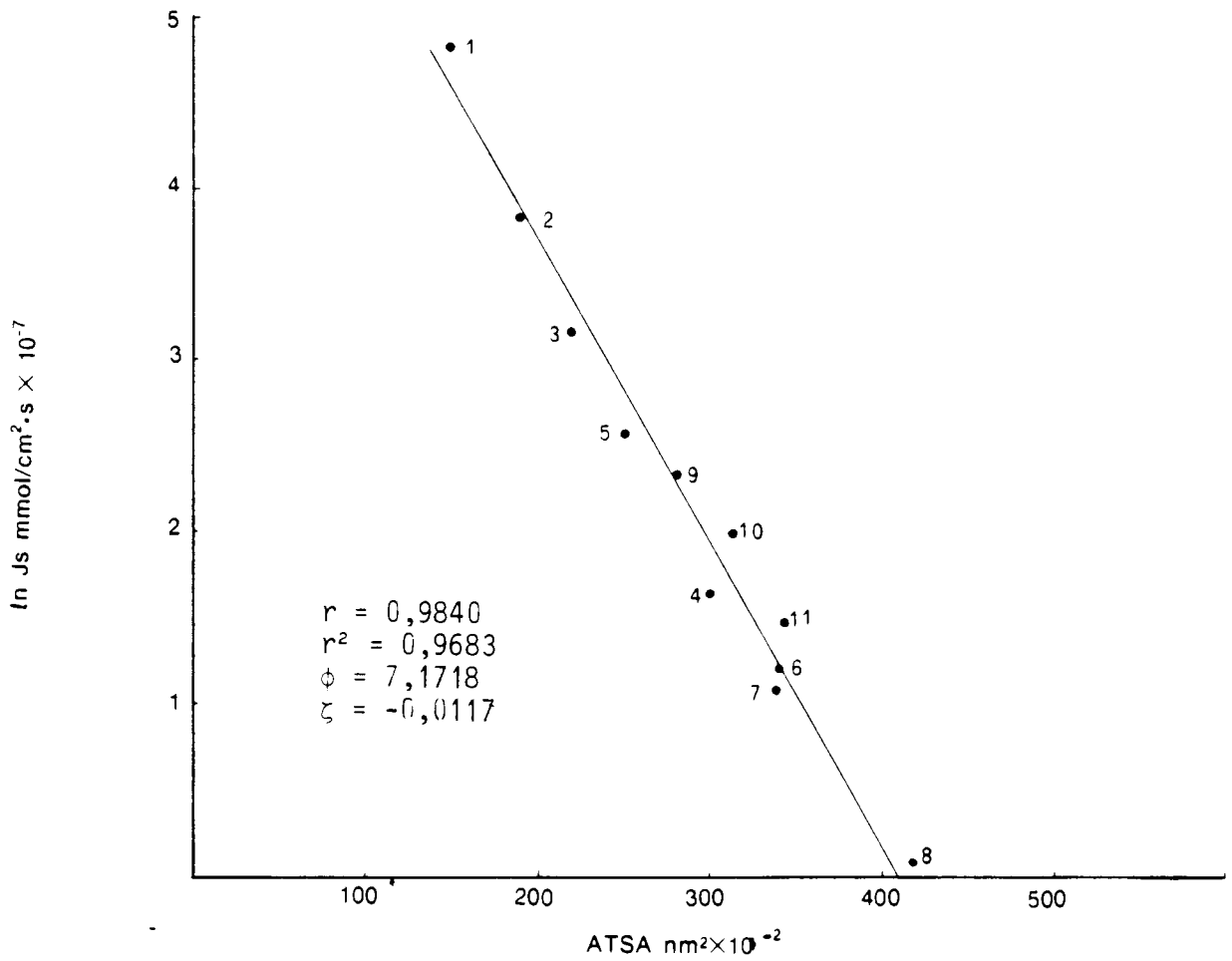


FIGURE 4.35: SOLUTE FLUX vs. ADJUSTED TOTAL CAVITY SURFACE AREA (ATSA); FT-30 ALCOHOLS (SOLUTE NUMBERS IN TABLE 4.13)

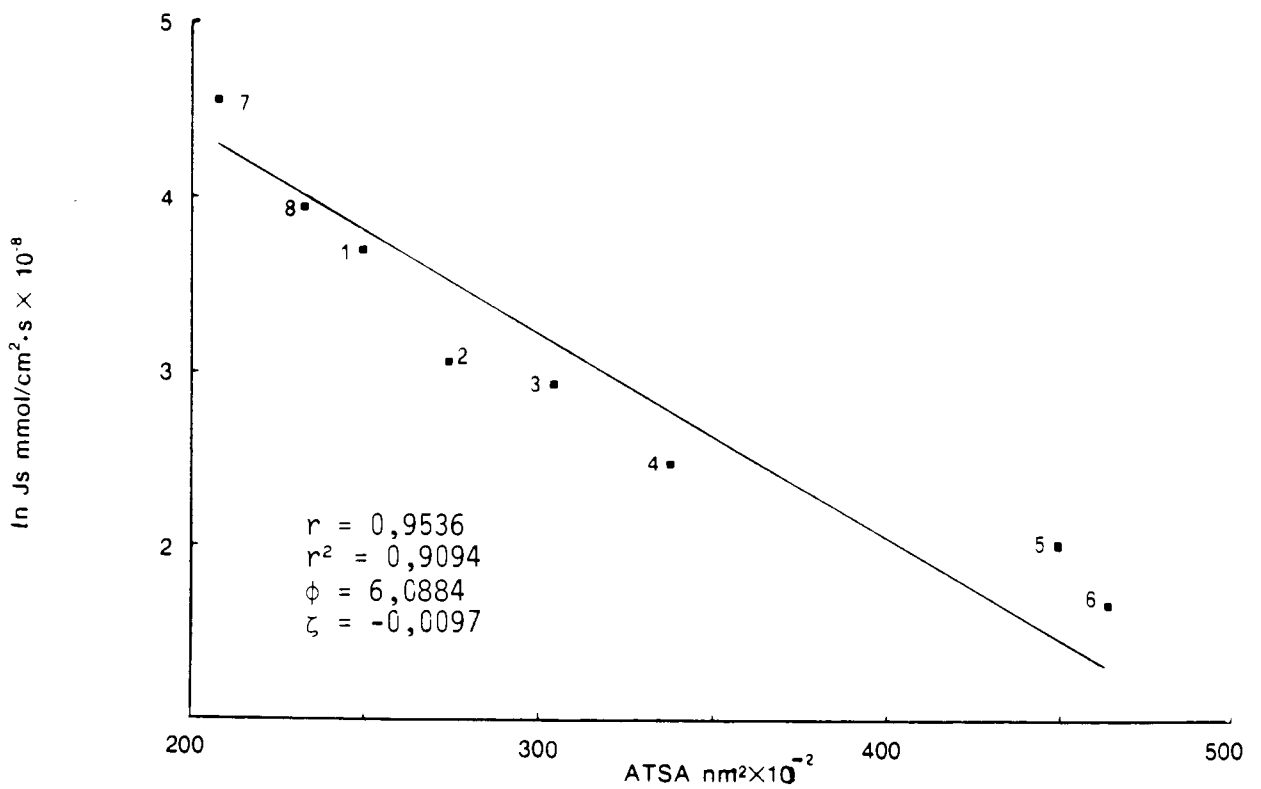


FIGURE 4.36: SOLUTE FLUX vs. ADJUSTED TOTAL CAVITY SURFACE AREA (ATSA); FT-30; PHENOLS (SOLUTE NUMBERS IN TABLE 4.14)

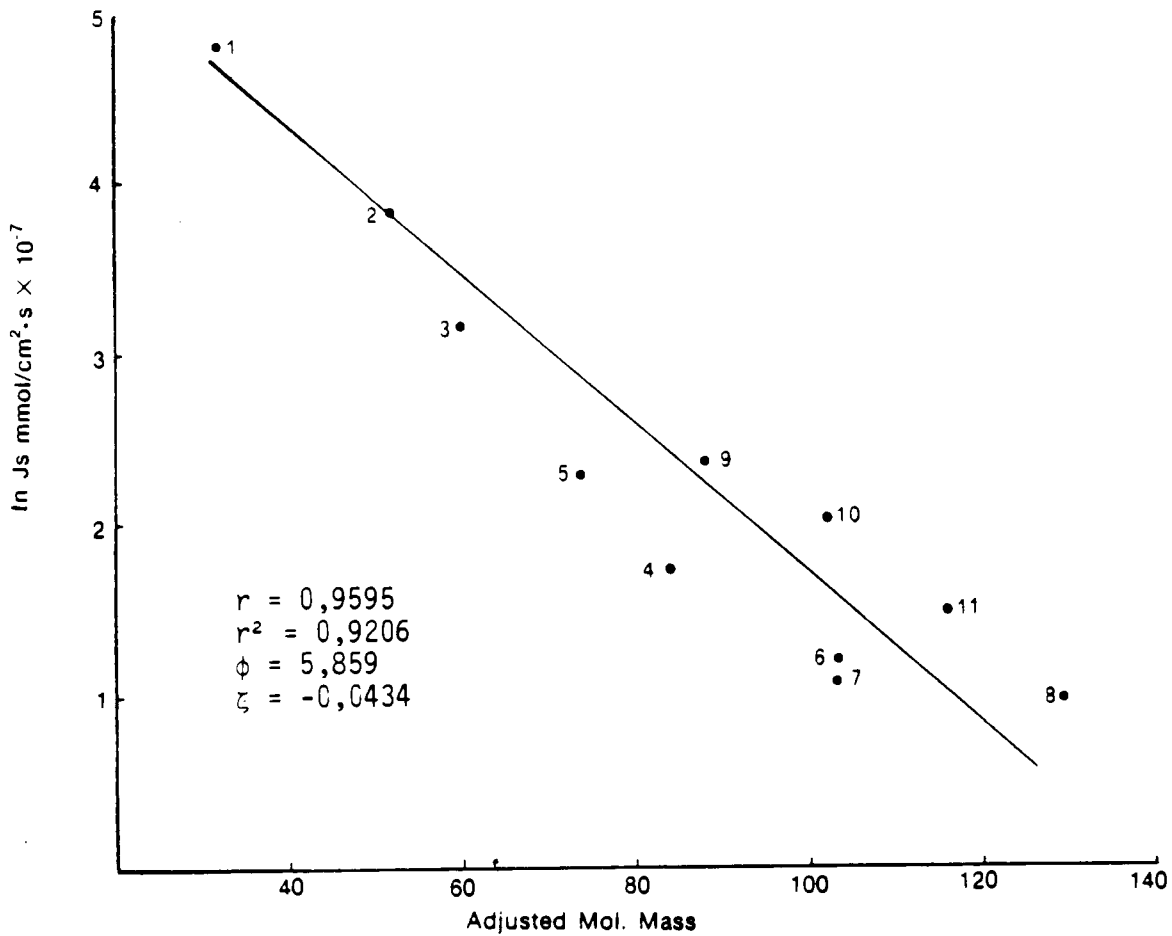


FIGURE 4.37: SOLUTE FLUX vs. ADJUSTED MOLECULAR MASS; FT-30; ALCOHOLS (SOLUTE NUMBERS IN TABLE 4.13)

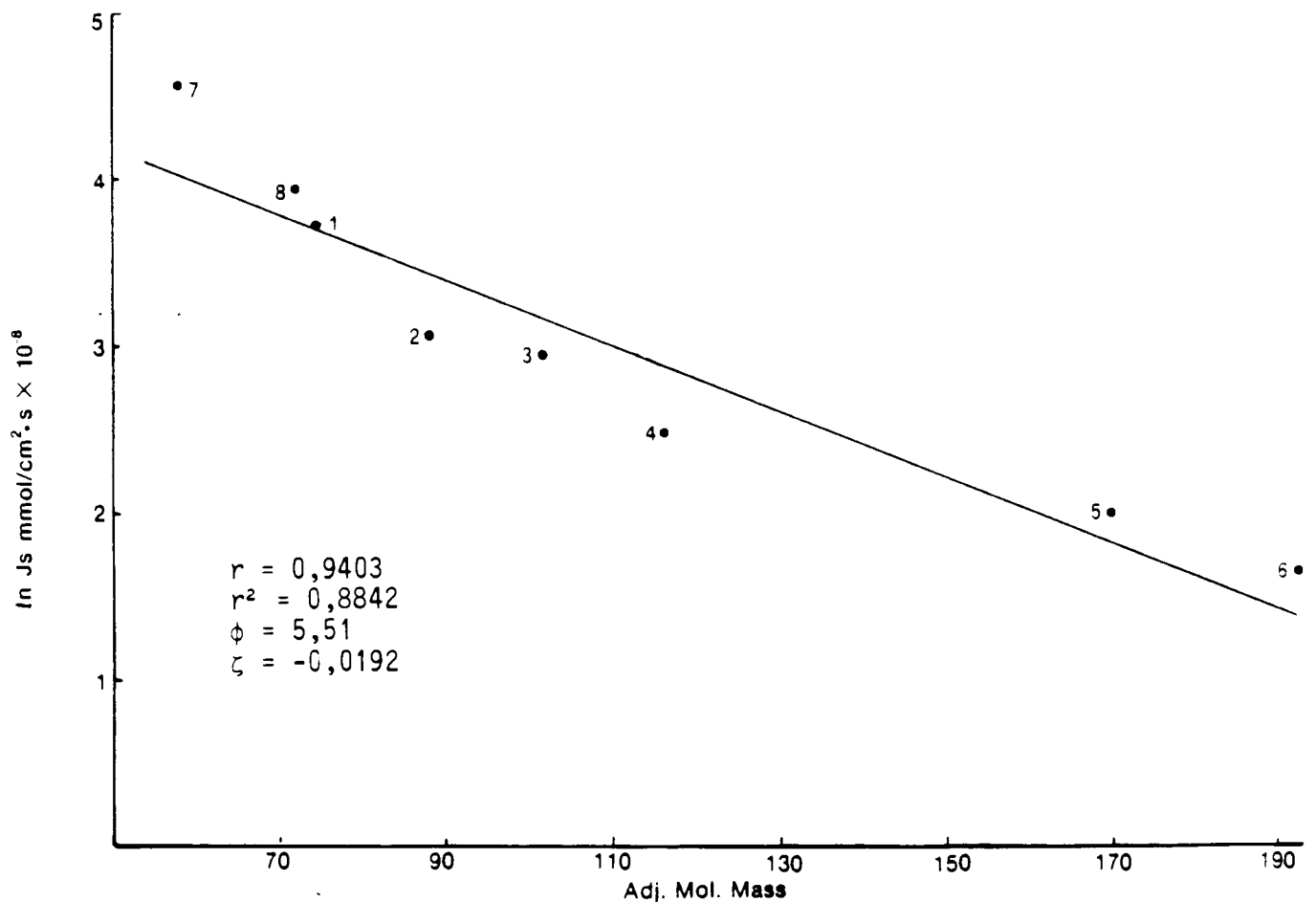


FIGURE 4.38: SOLUTE FLUX vs. ADJUSTED MOLECULAR MASS; FT-30; PHENOLS (SOLUTE NUMBERS IN TABLE 4.14)

lower than the coefficients for total cavity surface area indicating that the factor for hydrodynamic shape does not account fully for the effect of branching in correlations with molecular mass. It should be noted, however, that experimental solute fluxes for the branched isomers are consistently below the regression line indicating that this model consistently predicts higher solute fluxes and therefore lower rejections for branched isomers than are obtained experimentally. This means that in practice higher rejections will be achieved than predicted by the model.

In summary, the model based on the simplified solvophobic theory correlates extremely well with experimental data. This indicates that the interactions as described by the solvophobic theory and the simplification thereof give a good representation of solute-solvent-membrane interactions, while the factor based on the ratio of cross-sectional areas adequately accounts for differences in hydrodynamic shape effects, for the relatively non-polar composite FT-30 membrane.

The use of molecular mass in the further simplification of the model has a firm theoretical basis in the solvophobic theory, while earlier correlations of this nature were based on empirical observations related to size effects (Duvel and Helfgott 1975).

The main advantage of this model is that it is very simple and easy to use and that input data are readily available. The main limitations are that the model is restricted to relatively non-polar membranes and furthermore, that it is not entirely predictive since some experimental data is required for membranes with different characteristics in order to establish basic correlations.

4.8 CONCLUSIONS

- (i) A review of membrane models indicated that models based on the thermodynamics of irreversible processes are not suitable for the purpose of this study, i.e. they cannot be used in a simple predictive way to determine the rejection of different organics by reverse osmosis membranes. These models do, however, allow analysis of reverse osmosis data and prediction of solute and solvent flux based on certain coefficients derived from reverse osmosis data.
- (ii) The solution-diffusion model allows prediction of solute rejection based on the partitioning coefficient, K_s , and the diffusion coefficient, D_s of the particular organic solute and membrane. A detailed experimental study was conducted on the rejection of a series of alkyl alcohols and a series of alkyl phenols by an aromatic polyamide composite membrane (FT-30) and an asymmetric cellulose acetate membrane (SEPA-99). Further experimental data were obtained for the partitioning or sorption of phenol by these membranes and on the diffusion of phenol in these membranes.

K_s , D_s and $K_s D_s$ values were obtained from these experimental studies in order to verify the solution-diffusion model (Equation 4.49).

$$J_s = D_s K_s \frac{C_f - C_p}{\Delta x}$$

The $D_s K_s$ values obtained from reverse osmosis data and the $D_s K_s$ values obtained from determination of D_s and K_s in diffusion and sorption tests differed by about one order of magnitude for the FT-30 membrane :

$3,3 \times 10^{-6}$ cm²/s from reverse osmosis data and
 $8,3 \times 10^{-5}$ cm²/s from transient permeation and sorption tests
 and $1,8 \times 10^{-7}$ cm²/s from elution data and partitioning tests.

These data indicate fair agreement of the model with independent laboratory tests, if the experimental difficulties are taken into consideration.

For the SEPA-99 membrane the difference between the two sets of DSKs values is much smaller :

$1,9 \times 10^{-6}$ cm²/s from reverse osmosis data and
 $7,8 \times 10^{-6}$ cm²/s from partitioning and transient permeation data.

- (iii) The preferential sorption-capillary flow model allows calculation of solute rejection from physical-chemical data of solutes and a number of experimental coefficients and constants for the particular membrane. Reasonably good agreement was obtained between rejections predicted by the model and those found experimentally. This model does, however, not hold where solutes are preferentially sorbed by the membrane, for example it does not hold for phenols and higher alcohols. The model is not simple to use and it, therefore, does not meet the requirements of this study.
- (iv) A reasonable correlation was found between the rejection of alcohols by the FT-30 membrane and the total solubility parameter. However, no conclusion can be drawn with respect to rejection of phenols and solubility parameters.
- (v) The solvophobic theory was adapted in Section 4.3 for application to the rejection of organic compounds by reverse osmosis membranes. It was shown that the theory can be greatly simplified by the fact that the total cavity surface area can be used instead of the nett free energy change in association reactions such as the sorption of a solute from solution by a membrane. Transport effects are incorporated in the model through the diffusion coefficient which is also accounted for by the total cavity surface area and a factor to account for the hydrodynamic shape of the molecule.

Excellent correlations were found between solute flux and the simplified solvophobic model for both the series of alcohols and the series of phenols and the FT-30 membrane.

- (vi) In order to further simplify this model the total cavity surface area was replaced by molecular mass since a linear relationship between molecular mass and TSA exists for linear compounds. Reasonably good correlations were found between solute flux and molecular mass adjusted for differences in diffusion coefficient, and the FT-30 membrane.

- (vii) It was concluded from diffusion and sorption tests that phenol interacts more strongly with the composite polyamide membrane than with the cellulose acetate membrane, resulting in larger sorption by the composite membrane, stronger forces of attraction, lower rates of diffusion and, therefore, good rejection of phenol by the FT-30 membrane compared to poor rejection by the cellulose acetate membrane.

CHAPTER 5

GENERAL CONCLUSIONS AND RECOMMENDATIONS

5.1 GENERAL CONCLUSIONS

The following main conclusions can be drawn from this study :

- (i) A significant potential role was found to exist for reverse osmosis in the South African water economy. These potential applications fall in four categories, i.e.
- The treatment of industrial effluents, and the reclamation of water from industrial effluents. The biggest potential applications of reverse osmosis in the short to medium term fall in this category. Potential applications include the treatment of cooling water blow down, the treatment of effluents from chemical and metallurgical industries, from food processing industries and the treatment and reclamation of underground mine waters.
 - Desalination of brackish water. Current and projected shortages in the water supply to many small communities as well as a number of larger towns including De Aar and Graaff-Reinet could be met by desalination of available brackish water sources.
 - A potential role for reverse osmosis is being projected for the reclamation of water of very good quality for direct reuse in municipal supplies. Potential applications are projected towards the turn of the century at a number of locations including Cape Town and Pietersburg.
 - The treatment of effluents and recycled water in indirect reuse situations. Potential applications in this category are projected for indirect reuse situations where the quality of water sources is deteriorating as a result of relatively high rates of indirect water recycling.

5.2

- Desalination of sea water on large scale is not expected to become economically viable in the South African water supply situation within the next ten to fifteen years.
- (ii) It was concluded from a desk study that reverse osmosis as a water reclamation process could become economically viable in some water reuse situations in the near future. Estimated reclamation costs of between R0,70 and R0,80 per cubic meter are markedly higher than current costs to produce water from conventional sources. These estimated costs could become competitive with incremental water supply costs where additional water has to be supplied by means of importation of water from other catchments.
- (iii) Pilot plant studies and a literature study indicated that reverse osmosis will be technically feasible in water reclamation applications. It was concluded from these studies that design membrane fluxes can be maintained in tubular reverse osmosis plants treating activated sludge effluent, provided both physical and chemical cleaning procedures are employed. Reclaimed water of very good quality can be produced by reverse osmosis but additional post treatment is required for the removal of very small quantities of organics which permeate the membranes. Post disinfection will also be required if the reclaimed water is to be considered for potable reuse.
- (iv) Desk and pilot plant studies indicated the need for a simple model that can be used to predict the removal of organic compounds by reverse osmosis membranes in water reclamation applications. It was concluded from a fundamental study on these aspects that the solvophobic theory can be adapted in a much simplified form for this purpose. The nett free energy change in the association reaction between an organic molecule and an active site in a membrane can be represented by the total cavity surface area of the solute. Transport

5.3

phenomena can be incorporated in the model by adjusting the total cavity surface area by a factor based on the molecular structure of the solute molecule. This correction factor accounts for differences in the diffusion coefficients of different solutes in a particular membrane. The following very simple model was developed and tested for solute transport in a membrane

$$\ln J_s = \phi + \zeta \sqrt{Axs} \text{ (TSA)}$$

This model was shown to correlate very well with experimental data on two series of organic compounds and a relatively non-polar reverse osmosis membrane.

It was furthermore shown that this model can be simplified even further by using solute molecular mass instead of total cavity surface area to represent the solvophobic interactions.

- (v) It was concluded from reverse osmosis data, sorption and desorption studies, and diffusion experiments that phenol is highly sorbed by aromatic polyamide and that relatively strong forces of attraction exist between phenol and the aromatic polyamide membrane. This results in a low rate of diffusion and good rejection by the membrane. In contrast, the forces of attraction between phenol and cellulose acetate are relatively weak, resulting in a high rate of diffusion and poor rejection of phenol by cellulose acetate membranes.

5.2 RECOMMENDATIONS

It is recommended :

- (i) That a relatively small reverse osmosis plant be constructed in a practical water reclamation application in order to verify the findings of this study and to obtain design and operating criteria for large-scale applications.

5.4

- (ii) That experimental reverse osmosis data be obtained for a wider range of organic compounds of interest in water reclamation applications to evaluate the predictive model developed in this study on a wider basis.

- (iii) That, in view of the superior characteristics of composite membranes, local research and development efforts be concentrated on the development of a relatively non-polar tubular composite reverse osmosis membrane for use in water reclamation applications.

A1

APPENDIX A

DATA FROM PILOT PLANT RECLAMATION STUDIES

Table A1 - BENCH SCALE COAGULATION/FLOCCULATION TESTS
USING FERRIC CHLORIDE AT VARYING pH LEVELS

pH	Fe mg/ℓ	Plugging Index (15) *	S.D.I. (15)	M.F.I. sec/ℓ ²	UV Absorbance 275 nm	UV Absorbance 254-545 nm	Residual Fe mg/ℓ
7,4	0	-	-	-	0,234	0,261	0,02
7,0	10	89	5,9	91,9	0,215	0,239	0,02
7,0	15	90	6,0	32,3	0,208	0,233	0,04
7,0	20	94	6,2	21,3	0,203	0,224	0,05
7,0	25	92	6,1	17,1	0,196	0,220	0,02
7,0	30	90	6,0	19,3	0,188	0,209	0,02
7,0	35	94	6,3	14,2	0,165	0,185	0,04
6,5	10	96	6,4	46,5	0,200	0,224	0,04
6,5	15	81	5,4	13,3	0,193	0,214	0,05
6,5	20	84	5,6	15,8	0,193	0,199	0,04
6,5	25	78	5,2	12,4	0,161	0,171	0,03
6,5	30	78	5,2	11,4	0,166	0,189	0,04
6,5	35	79	5,3	11,6	0,158	0,173	0,04
6,0	10	87	5,8	13,9	0,197	0,218	0,04
6,0	15	83	5,5	11,0	0,188	0,211	0,06
6,0	20	76	5,1	6,6	0,172	0,189	0,06
6,0	25	91	6,1	13,2	-	-	-
6,0	30	88	5,9	10,4	-	-	-
6,0	35	81	5,4	5,6	-	-	-
5,5	10	95	6,3	80,4	0,188	0,205	0,10
5,5	15	93	6,2	32,5	0,170	0,186	0,09
5,5	20	91	6,1	12,8	0,156	0,168	0,10
5,5	25	85	5,7	12,1	0,137	0,148	0,12
5,5	30	70	4,7	3,8	0,134	0,129	0,09
5,5	35	72	4,8	4,7	0,124	0,128	0,11
5,0	10	92	6,2	28,2	0,190	0,210	0,12
5,0	15	74	4,9	6,6	0,167	0,178	0,10
5,0	20	77	5,1	6,7	0,137	0,149	0,15
5,0	25	-	-	1,9	0,118	0,123	0,22
5,0	30	-	-	1,1	0,115	0,123	0,16
5,0	35	-	-	1,5	0,105	0,113	0,20

TABLE A2 TESTS USING FERRIC CHLORIDE AS COAGULANT, AT VARIOUS pH LEVELS

RAW FEED WATER		COAGULATION CONDITIONS		DAF EFFLUENT						MMF EFFLUENT					
Turbidity NTU	UV Abs 275 nm	Fe mg/l	pH in Flocculator	Fe Added mg/l	Unfilt.			3 μ Filtered			Turbidity NTU	FI (15) %	MFI sec ℓ^{-2}	UR Abs. 275 nm	Residual Fe mg/l
					Turbidity NTU	FI (15) %	MFI sec ℓ^{-2}	UV Abs 275 nm	Residual Fe mg/l						
0,90	0,265	0,10	6,5	20	2,5	-	-	-	0,80	-	-	-	-	-	-
0,85	0,225	0,08	6,5	25	1,6	-	-	-	0,33	-	-	-	-	-	-
0,80	0,211	0,12	6,0	20	0,58	94,5	20,9	0,185	0,20	28,4	0,80	0,140	0,10	0,10	
0,95	0,223	0,02	6,0	25	0,21	95,5	9,6	0,200	0,19	39,0	0,73	0,121	0,08	0,08	
0,76	0,216	0,07	6,0	30	0,21	77,1	5,6	0,158	0,18	33,9	1,02	0,115	0,08	0,08	
0,64	0,214	0,07	5,5	20	0,24	78,7	5,1	0,185	0,19	17,3	0,28	0,122	0,10	0,10	
1,0	0,281	0,12	5,5	25	0,18	75,9	3,1	0,170	0,17	4,0	0,12	0,110	0,06	0,06	
0,70	0,220	0,11	5,5	30	0,18	52,7	1,8	0,145	0,16	0,7	0,07	0,080	0,10	0,10	

OPERATING CONDITIONS: 40 ℓ /min Feed

10-6-2 rpm on baffles

10 % recycle on DAF.

Table A4 TESTS ON VARYING THE RECYCLE/FEED PERCENTAGE ON D A F UNIT

RAW FEED WATER			D A F EFFLUENT				M M F EFFLUENT							
Turbidity NTU	UV Abs 275 nm	Fe mg/ℓ	RECYCLE		UNFILT		3μ FILTERED			Turbidity NTU	FI(15) %	MFI sec ℓ ⁻²	AU Abs 275 nm	Residual FE mg/ℓ
			ON D A F %	ON D A F %	Turbidity NTU	FI(15) %	MFI sec ℓ ⁻²	UV Abs 275 nm	Residual Fe mg/ℓ					
0,64	0,214	0,02	5	5	0,44	72,4	6,48	0,155	0,11	0,17	29,4	0,71	0,115	0,05
0,82	0,208	0,05	7,5	7,5	0,50	85,1	8,45	0,159	0,08	0,18	34,3	0,82	0,109	0,04
0,63	0,220	0,11	10	10	0,45	49,1	2,41	0,127	0,04	0,16	18,4	0,46	0,113	0,02
0,84	0,215	0,20	12,5	12,5	0,18	65,5	2,69	0,118	0,09	0,18	33,1	0,97	0,106	0,05

OPERATING CONDITIONS : 40 ℓ/min Feed
20 mg/ℓ Fe
10-6-2 rpm on baffles
pH 5,5 in flocculator

Table A3 TESTS USING FERRIC CHLORIDE WITH POLYELECTROLYTE (C573)

RAW FEED WATER		COAGULATION CONDITIONS			D A F EFFLUENT				M M F EFFLUENT						
Turbidity NTU	UV Abs 275 mm	Fe mg/ℓ	C573 Poly-mg/ℓ	Fe mg/ℓ	pH	3μ FILTERED				Turbidity NTU	FI(15) %	MFI sec/ℓ	UV Abs 275 mm	Residual mg/ℓ	
						Turbidity NTU	FI(15) %	MFI sec ℓ ⁻²	UV Abs 275 mm						Residual Fe mg/ℓ
0,65	0,211	0,12	0,5	20	5,5	0,46	78,0	2,07	0,122	0,10	0,12	12,1	0,36	0,094	0,07
0,96	0,219	0,08	1,0	20	5,5	0,62	69,7	2,77	0,121	0,09	0,13	34,3	0,89	0,105	0,05
0,50	0,216	0,03	1,5	20	5,5	0,54	59,0	2,48	0,133	0,07	0,15	15,4	0,74	0,107	0,04
0,65	0,212	0,03	2,0	20	5,5	0,68	21,2	0,94	0,114	0,18	0,16	27,2	0,69	0,103	0,11
OPERATING CONDITIONS : 40 ℓ/min Feed					10-6-2 rpm on baffles					10% Recycle on D A F					

Table A5 ANALYSES OF SAMPLES TAKEN DURING EXTENDED TEST - USING ONLY FERRIC CHLORIDE

		UNTREATED FEED	DAF EFFLUENT	MMF EFFLUENT
Na	mg/l	86,4	86,8	91,0
K	mg/l	13,8	14,1	14,1
Ca	mg/l	39,1	49,8	68,9
Mg	mg/l	4,3	4,5	5,1
Cd	mg/l	<0,01	<0,01	<0,01
Sr	mg/l	0,10	0,18	0,22
Fe	mg/l	<0,02	0,18	0,02
NH ₃ as N	mg/l	0,1	0,2	0,1
SO ₄	mg/l	80	126	131
Cl	mg/l	84	123	128
Alkalinity as CaCO ₃	mg/l	111	41	89
NO ₂ + NO ₃ as N	mg/l	1,8	1,7	1,8
PO ₄ as P	mg/l	1,8	<0,1	<0,1
COD	mg/l	36	32	44
Absorbance UV 275nm		0,239	0,119	0,108
Absorbance UV 254nm		0,296	0,147	0,137
Absorbance (UV ₂₅₄ - VIS ₅₄₅) (All 1cm path length)		0,264	0,122	0,113
pH		7,4	5,5	5,6
Conductivity	mS/m	70	75	76
MFI	sec l ⁻²	-	10,1	0,56
Fouling Index (15 min)	%	-	87,5	17,5
Turbidity	NTU	0,46	0,59	0,10

Table A6 ANALYSES OF SAMPLES TAKEN DURING EXTENDED TEST - USING FERRIC CHLORIDE AND C573 POLYELECTROLYTE

		UNTREATED FEED	DAF EFFLUENT	MMF EFFLUENT
Na	mg/l	89,6	88,2	90,3
K	mg/l	14,5	14,5	14,4
Ca	mg/l	36,3	34,2	34,2
Mg	mg/l	3,8	3,7	3,7
Cd	mg/l	<0,01	<0,01	<0,01
Sr	mg/l	0,07	0,10	0,10
Fe	mg/l	<0,02	<0,05	<0,02
NH ₃ as N	mg/l	0,2	0,1	0,1
SO ₄	mg/l	77	130	127
Cl	mg/l	82	106	110
Alkalinity as CaCO ₃	mg/l	106	24	30
NO ₂ + NO ₃ as N	mg/l	2,2	2,1	1,9
PO ₄ as P	mg/l	4,2	<0,1	<0,1
COD	mg/l	40	40	44
Absorbance UV 275nm		0,214	0,155	0,115
Absorbance UV 254nm		0,269	0,195	0,154
Absorbance (UV ₂₅₄ - VIS ₅₄₅) (All 1cm path length)		0,239	0,171	0,131
pH		7,3	5,7	6,0
Conductivity	mS/m	68	73	75
MFI	sec l ⁻²	-	5,68	0,75
Fouling Index (15 min)	%	-	61,7	21,5
Turbidity	NTU	0,61	0,47	0,15

Table A7 : Analyses of Samples - Pretreatment

Date Sampled	28-06-1983				26-07-1983				23-08-1983				20-09-1983			
	Raw Feed	DAF	MMF	% Re-duction	Raw Feed	DAF	MMF	% Re-duction	Raw Feed	DAF	MMF	% Re-duction	Raw Feed	DAF	MMF	% Re-duction
K	mg/l	13,8	13,8	0	14,4	14,2	14,2	1,4	14,3	14,2	14,2	0,9	13,9	13,2	13,5	2,9
Na	mg/l	78,0	78,0	- 6,0	93,9	93,2	94,6	- 0,8	94	90	96	- 2,1	98	97	106	- 8,2
Ca	mg/l	52,6	51,9	2,3	53,3	53,3	53,7	- 0,8	50	50	50	0	46	46	46	0
Mg	mg/l	8,7	8,6	2,3	9,2	9,2	9,5	- 3,3	8,8	8,5	8,5	3,4	9	9	9	0
NH ₃ -N	mg/l	0,2	0,2	0	<0,1	<0,1	<0,1	0	0,2	0,1	0,1	50,0	0,2	0,2	0,2	0
Fe	mg/l	-	-	-	0,05	0,67	0,07	-	0,04	0,97	0,05	-	0,06	1,14	0,07	-
SO ₄	mg/l	80	124	-53,8	89	136	140	-57,3	100	135	133	-33,0	91	141	140	-53,9
Cl	mg/l	92	130	-45,7	102	147	147	-44,1	101	143	148	-46,5	102	148	153	-50,0
Alkalinity as CaCO ₃	mg/l	106	14	84,0	124	16	17	86,3	97	13	14	85,6	118	15	18	84,8
NO ₂ + NO ₃ - N	mg/l	7,4	7,4	10,8	5,4	5,4	5,4	0	9,1	9,1	8,8	3,3	5,5	5,5	5,4	1,8
P (reactive)	mg/l	2,73	0,08	98,5	1,5	<0,1	<0,1	93,3	4,5	0,1	0,1	97,8	2,5	0,1	0,1	96,0
TDS Calculated	mg/l	496	457	6,5	542	497	504	6,9	541	497	506	6,5	536	497	513	4,14
COD	mg/l	52	(20)	23,1	32	16	24	25,0	40	28	28	30,0	40	22	20	50,0
TOC	mg/l	10,4	5,0	51,9	11,2	6,4	6,0	46,4	12,6	6,6	7,4	41,3	9,8	6,0	5,8	40,8
Absorbance UV275nm		0,199	0,103	0,086	0,235	0,097	0,075	-	0,242	0,142	0,098	-	0,275	0,177	0,142	-
Absorbance (UV275-VIS545)		0,212	0,097	0,084	0,276	0,087	0,067	-	0,279	0,155	0,106	-	0,300	0,153	0,168	-
Conductivity	mS/m	62	77	80	83	89	90	-8,43	80	85	88	-10,0	79	86	89	-12,7
pH		7,3	5,8	5,9	7,2	5,5	5,6	-	7,3	5,5	5,7	-	7,1	5,7	5,9	-
MFI	sec/l ²	-	-	0,15	-	-	1,74	-	-	-	0,75	-	-	-	1,84	-
FI (15)	%	-	-	15,6	-	-	47,9	-	-	-	21,8	-	-	-	37,8	-
SDI (15)		-	-	1,0	-	-	3,2	-	-	-	1,5	-	-	-	2,5	-
Turbidity	FTU	0,38	0,76	0,21	0,67	1,04	0,11	-	0,6	0,88	0,14	-	0,42	1,4	0,14	-

Table A8 Analyses of Samples - Pretreatment

Date Sampled	29-09-1983					4-10-1983					18-10-1983					17-11-1983				
	Raw Feed	DAF	MMF	% Re-duction		Raw Feed	DAF	MMF	% Re-duction		Raw Feed	DAF	MMF	% Re-duction		Raw Feed	DAF	MMF	% Re-duction	
K	mg/l	15,6	15,6	1,3		15,6	15,6	15,6	0		15,2	-	15,2	0		14,7	-	14,3	2,7	
Na	mg/l	87	88	-11,5		83	83	89	-7,2		76,8	-	81,0	-5,5		94,3	-	94,8	-0,5	
Ca	mg/l	48	47	-		48	(86)	48	0		46,3	-	45,1	2,6		39,1	-	38,8	0,8	
Mg	mg/l	9	9	0		9	10	9	0		8,9	-	9,0	-1,1		5,1	-	5,5	-7,8	
NH ₃ -N	mg/l	0,1	0,1	0		0,1	0,1	0,1	0		0,23	-	0,49	-113,0		0,09	-	0,15	-66,7	
Fe	mg/l	0,05	2,36	-		0,07	0,69	0,06	-		-	-	0,09	-		-	-	0,05	-	
SO ₄	mg/l	74	110	-56,8		71	90	92	-29,6		64	-	92	-43,8		97	-	115	-18,6	
Cl	mg/l	97	147	-62,9		94	147	149	-58,5		93	-	140	-50,5		83	-	147	-77,1	
Alkalinity as CaCO ₃	mg/l	94	9	12,8		84	(119)	9	89,3		85	-	13	84,7		104	-	13	87,5	
NO ₂ + NO ₃ - N	mg/l	7,0	7,6	1,43		11,9	12,3	11,8	0,8		10,3	-	10,0	2,9		2,8	-	2,4	14,3	
P (Reactive)	mg/l	5,5	0,1	98,2		5,9	0,1	0,1	98,3		6,2	-	<0,1	98,4		3,6	-	<0,1	97,2	
TDS Calculated	mg/l	493	462	-20,3		494	(632)	466	5,6		473	-	443	6,2		484	-	442	8,5	
COD	mg/l	32	18	31,3		28	14	22	21,4		36	-	16	55,6		48	-	28	41,7	
TOC	mg/l	11,0	6,8	40,0		9,4	5,4	5,8	38,3		8,8	-	5,4	38,6		10,4	-	5,8	44,2	
Absorbance UV275nm		0,272	0,155	0,131		0,237	0,116	0,108	-		0,239	-	0,158	0,144		0,273	-	0,148	0,128	
Absorbance (UV275-VIS545)		0,297	0,144	0,138		0,252	0,106	0,098	-		0,236	-	0,137	0,125		0,273	-	0,125	0,110	
Conductivity	ms/m	79	85	-10,1		79	85	87	-10,1		70	-	78	-11,4		71	-	78	-9,9	
pH		7,2	5,6	5,7		7,3	5,5	5,8	-		7,2	-	5,75	-		7,3	-	5,8	-	
MFI	sec/l ²	-	-	2,05		-	-	1,53	-		-	-	0,79	-		-	-	1,34	-	
FI (15)	%	-	-	48,9		-	-	39,0	-		-	-	53,8	-		-	-	27,9	-	
SDI (15)		-	-	3,3		-	-	2,6	-		-	-	3,6	-		-	-	1,9	-	
Turbidity	FTU	0,66	0,76	0,15		0,42	0,87	0,10	-		0,70	-	0,75	0,12		1,6	-	0,88	0,11	

Table A9 C O D ANALYSES

Date 1983	Raw Feed mg/l	D.A.F. Effluent mg/l	M.M.F. Effluent mg/l	Bakke RO Permeate mg/l	Bakke RO Reject mg/l	PCI RO Feed mg/l	PCI RO Permeate mg/l	PCI RO Reject mg/l
10/06	64	-	24	12	92	-	-	-
14/06	24	-	20	<0	-	-	-	-
28/06	52	20	40	0	68	88	0	36
06/07	150	138	91	(28)	87	51	0	55
12/07	43	24	16	4	91	55	0	63
20/07	24	8	20	0	69	41	0	45
26/07	32	16	24	4	64	28	0	44
09/08	28	12	32	4	75	150	0	79
16/08	27	19	27	4	64	44	0	44
23/08	40	23	28	8	109	65	0	60
30/08	36	24	24	4	84	64	0	84
06/09	35	23	28	4	153	75	0	78
13/09	33	13	16	0	69	65	0	69
20/09	40	22	20	0	100	72	0	66
27/09	32	13	22	4	92	80	0	60
04/10	28	14	22	4	60	60	0	60
18/10	36	-	16	4	83	56	6	60
17/11	48	-	28	8	83	72	6	89
22/11	46	-	28	6	71	44	8	99
23/11	-	-	32	6	91	-	-	-
06/12	36	-	20	0	89	64	0	97
13/12	30	-	24	(32)	103	91	4	93

Table A10 T O C ANALYSES

Date 1983	Raw Feed mg/l	D.A.F. Effluent mg/l	M.M.F. Effluent mg/l	Bakke RO Permeate mg/l	Bakke RO Reject mg/l	PCI RO Feed mg/l	PCI RO Permeate mg/l	PCI RO Reject mg/l
28/06	10,4	5,0	5,0	0,6	14,0	11,0	0,6	11,8
12/07	13,4	5,8	6,0	1,0	14,6	13,0	0,2	14,0
26/07	11,2	6,4	6,0	0,8	12,0	9,8	0,0	10,0
09/08	12,0	6,4	6,4	0,8	16,6	14,2	0,0	14,4
23/08	12,6	6,6	7,4	0,8	11,6	11,6	0,4	12,0
20/09	9,8	6,0	5,8	0,8	20,4	15,2	0,2	15,0
27/9	11,0	6,8	6,6	<1,0	>20,0	17,2	<1,0	18,2
04/10	9,4	5,4	5,8	1,0	13,2	12,2	1,0	12,4
18/10	8,8	5,8	5,4	1,0	12,6	11,8	1,2	11,4
03/11	10,4	5,8	5,8	1,8	18,4	17,8	1,0	19,4
22/11	9,2	5,4	5,0	0,4	13,4	13,2	0,6	12,8
06/12	10,8	6,4	6,4	1,6	17,2	15,2	1,6	15,4
13/12	9,8	6,4	6,2	<1,0	24,0	20,8	2,0	25,0

Table A11 BAKKE RO UNIT - MEMBRANE CLEANING PROCEDURES

Date 1983	Total Hours	Membrane Cleaning Procedure		Pre-clean Flux			Post-clean Flux	
		Cleaning material used/ Remarks	Duration Min	pH	Actual Flux $\ell.m^{-2}.d^{-1}$	Corrected Flux $\ell.m^{-2}.d^{-1}$	Actual Flux $\ell.m^{-2}.d^{-1}$	Corrected Flux $\ell.m^{-2}.d^{-1}$
20/06	331	2% Citric Acid + NH_4OH	90	3,5	531	772	599	926
04/07	662	2% Citric Acid + NH_4OH	80	3,5	568	750	644	909
18/07	999	2% Citric Acid + NH_4OH	60	3,5	568	745	639	849
08/08	1504	2% Citric Acid + NH_4OH	145	3,5	577	742	680	902
22/08	1839	2% Citric Acid + 0,1 Biotex	130	3,5	514	624	672	902
05/09	2174	2% Biotex 2% Citric Acid + 0,02% Biotex + NH_4OH	110 120	9,0 3,5	538	686	680	898
19/09	2511	2% Citric Acid + NH_4OH 2% Biotex	120 110	3,5 9,0	638	845	745	1014
03/10	2846	2% Citric Acid + 0,1% Biotex + NH_4OH	180	3,5	633	816	700	946
06/10	2920	Convert to 26 Modules	-	-	-	-	-	-
31/10	3519	2% Citric Acid + 0,5% Ultrasil 50 + NH_4OH	165	3,5	769	849	871	1036
29/11	4215	2% Citric Acid + NH_4OH	105	3,5	739	1025	1046	975
30/11	4243	Convert to 20 Modules	-	-	-	-	-	-
12/12	4527	2% Citric Acid + 0,5% Ultrasil 50 + NH_4OH	90	4,2	942	877	1020	942

Table A12 Composite module : cleaning procedures

Date	Project Duration	Membrane Cleaning Procedure			Pre-clean Flux		Post-clean Flux	
		Cleaning material used/ REMARKS	Duration Minutes	Temp. Range °C	Actual Flux $\ell.m^{-2}.d^{-1}$	Corrected Flux $\ell.m^{-2}.d^{-1}$	Actual Flux $\ell.m^{-2}.d^{-1}$	Corrected Flux $\ell.m^{-2}.d^{-1}$
1983	Hours							
27/06	144	2% Biotex	105	15-28	690	763	704	733
28/06	170	2% Citric + NH_4OH (pH 3,5)	60	15-23	675	704	562	580
29/06	193	0,3% HNO_3	60	43-41	557	582	718	750
		0,25% NaOH	60	42-41				
06/07	359	0,3% HNO_3	30	40-35	516	552	598	660
		0,25% NaOH	120	18-35				
19/07	673	0,4% HNO_3	60	45-40	522	550	626	653
		0,4% NaOH	60	48-45				
08/08	1151	0,3% HNO_3	120	23-32	531	564	547	571
		0,5% NaOH	120	38-40				
16/08	1340	0,4% HNO_3	100	46-41	535	546	637	657
		0,4% NaOH	100	39-42				
		0,05% H_2O_2	60	20-27				
22/08	1487	0,4% HNO_3	140	46-40	526	546	561	592
		0,5% NaOH	90	43-41				
		0,05% H_2O_2	45	17-23				
29/08	1653	0,25% NaOH + 0,25% Ultrasil 50	140	47-37	487	508	577	590
05/09	1820	0,5% Ultrasil Introduce sponge balls	30	40-34	440	512	448	449
07/09	1869	0,4% HNO_3	120	45-38	459	472	557	565
		0,4% NaOH	160	40-36				
12/09	1989	0,4% HNO_3	90	48-41	538	545	609	605
		0,4% NaOH	180	37-42				
19/09	2157	0,4% HNO_3	120	50-42	524	531	610	605
		0,4% NaOH	140	42-36				
26/09	2324	0,5% HNO_3	180	43-36	528	520	533	519
		0,5% NaOH	150	50-44				
03/10	2492	0,4% HNO_3	120	52-42	497	521	641	640
		0,4% NaOH	170	37-42				
11/10	2684	0,4% HNO_3	180	47-43	573	611	689	754
		0,4% NaOH	140	52-47				
31/10	3167	0,4% HNO_3	180	49-41	599	551	731	666
		0,4% NaOH	75	50-42				
15/11	3527	0,5% HNO_3	130	37-41	593	516	904	775
		0,5% NaOH	140	47-43				
28/11	3839	0,5% HNO_3	120	51-47	879	741	1194	966
		0,5% NaOH	110	44-41				
12/12	4173	0,4% HNO_3	105	50-40	875	709	1425	1131
		0,4% NaOH	120	42-43				

Table A13 2% Cold water Biotex, determine effect of short exposures (new membranes)

24.1h COMPACTION AT 1960 mg/l NaCl, 25°C, 4.1 MPa, 1.5 m/s, pH6						
Rejection (%) flux (lmd)	96,3 800	96,6 720	96,4 740	96,9 750		96,7 740
2h, 2% COLD WATER BIOTEX WASH AT 25°C, 500 kPa, 1.5 m/s, pH9						
0,8 h STANDARDIZATION AT 1940 mg/l NaCl, 25°C, 4,1 MPa, 1,5 m/s, pH6						
Rejection flux	96,2 830	96,8 790	96,3 810	96,1 680	96,7 760	96,9 670
4,4h, 2% COLD WATER BIOTEX WASH AT 25°C, 500 kPa, 1.5 m/s, pH9						
0,5h STANDARDIZATION AT 1940 mg/l NaCl, 25°C, 4,1 MPa, 1,5 m/s, pH6						
Rejection flux	96,0 800	96,5 790	96,1 770	96,7 750	96,4 780	96,6 720
10h, 2% COLD WATER BIOTEX WASH AT 24°C, 500 kPa, 1.5 m/s, pH9						

2,7h STANDARDIZATION AT 1940 mg/l NaCl, 25°C, 4,1 MPa, 1,5 m/s, pH6						
Rejection (%) flux (lmd)	96,4 800	96,9 750	96,5 770	96,8 750	96,8 780	96,9 800

Table A14 4% Cold water Biotex - determine effect of short exposures (new membranes)

24h COMPACTION AT 2000 mg/l NaCl, 25°C, 4.1 MPa, 1,5 m/s, pH6						
Rejection (%)	96,0	96,2	96,9	97,2	96,6	97,3
Flux (lmd)	750	790	630	720	690	630
2,1h, 4% COLD WATER BIOTEX WASH AT 24°C, 500 kPa, 1,5 m/s, pH9						
0,7h STANDARDIZATION AT 1940 mg/l NaCl, 25°C, 4,1 MPa, 1,7 m/s, pH6						
Rejection	96,1	96,4	96,3	96,9	96,3	97,2
Flux	810	790	650	700	750	660
4h, 4% COLD WATER BIOTEX WASH AT 25°C, 500 kPa, 1,5 m/s, pH9						
0,7h STANDARDIZATION AT 1940 mg/l NaCl, 25°C, 4,1 MPa, 1,5 m/s, pH6						
Rejection	96,4	96,4	96,2	97,1	96,3	97,1
Flux	780	800	670	700	760	670
7,4h, 4% COLD WATER BIOTEX WASH AT 25°C, 500 MPa, 1,5 m/s, pH9						

0,5h STANDARIZATION AT 1930 mg/l NaCl 25°C, 4,1 MPa, 1,5 m/s, pH6						
Rejection (%)	96,2	96,5	96,1	97,0	96,4	97,2
Flux (lmd)	800	820	680	710	790	710
9,8h, 4% COLD WATER BIOTEX WASH AT 25°C, 500 MPa, 1,5 m/s, pH9						
0,4h STANDARDIZATION AT 1920 mg/l NaCl, 25°C, 4,1 MPa, 1,5 m/s, pH6						
Rejection	94,9	94,0	95,8	96,8	96,1	96,9
flux	800	750	680	724	780	660

Table A15 4% Cold water Biotex - determine effect of continued exposure (new membranes)

24,1h COMPACTION AT 2020 mg/l NaCl, 25°C, 4,1 MPa, 1,4 m/s, pH6						
Rejection (%) flux (lmd)	96,7 750	96,8 800	96,6 820	96,8 790	96,8 750	96,6 790
24,3h 4% COLD WATER BIOTEX WASH AT 25°C, 500 MPa, 1,2 m/s, pH9						
5,8h STANDARDIZATION AT 1960 mg/l NaCl, 25°C, 4,1 MPa, 1,4 m/s pH6						
Rejection flux	96,6 730	96,8 820	96,3 800	96,7 800	96,6 760	96,5 790

Table A16 6% Cold water Biotex - determine effect of continued exposure (new membranes)

22,2 h COMPACTION AT 2020 mg/l NaCl, 25°C, 4,1 MPa, 1,2 m/s, pH6						
Rejection (%)	96,9	96,4	96,1	97,1	95,6	96,5
flux (lmd)	740	790	710	680	730	760
24h, 6% COLD WATER BIOTEX WASH AT 25°C, 2 MPa, 1,3 m/s, pH9						
20,4h STANDARDIZATION AT 1980 mg/l NaCl, 25°C, 4,1 MPa, 1,3 m/s, pH6						
Rejection	96,2	97,0	96,5	97,5	97,4	97,0
flux	700	680	720	670	640	670

Table A17 5% citric acid, 0,5% Biotex, pH 3,5 (adjusted with NH₃OH) - continued exposure (new and used membranes)

23,5h COMPACTION AT 2130 mg/l NaCl, 25°C, 4,1 MPa, 1,2 m/s, pH6												
		MEMBRANES FROM MODULE 24						NEW MEMBRANES				
Rejection (%) flux (lmd)	73,1	79,6	78,5	84,2	80,3	81,8	96,4	97,5	97,3	95,5	96,7	96,6
	790	1250	1030	440	1310	1030	660	630	600	580	740	750
21,1h, 5% CITRIC ACID, 0,5% BIOTEX WASH AT 25°C, 2 MPa, 1,2 m/s, pH 3,5												
23,5h STANDARDIZATION AT 1930 mg/l NaCl, 24°C, 4,1 MPa, 1,3 m/s, pH 5,5												
Rejection flux	73,6	81,6	79,5	84,8	82,3	80,8	-	98,0	97,9	97,0	97,6	97,3
	670	1080	880	400	1180	940	-	580	550	540	700	720

Table A18 6% citric acid, 1,5% ultrasil, pH 3,5 (adjusted with NH₃OH) - continued exposure (new and used membranes)

23,3 COMPACTION AT 2030 mg/l NaCl, 25°C, 4,1 MPa, 1,2 m/s, pH6												
MEMBRANES FROM MODULE 24						NEW MEMBRANES						
Rejection (%)	86,7	75,8	75,8	80,6	82,5	84,5	98,1	97,5	97,4	97,0	97,1	96,8
flux (lmd)	1160	283	1560	1370	1430	1280	600	680	710	740	750	770
23,9h - 6% CITRIC ACID, 1,5% ULTRASIL, 25°C, 2 MPa, 1,3 m/s, pH 3,5												
23,9h - STANDARDIZATION AT 2020 mg/l NaCl, 25°C, 4,1 MPa, 1,1 m/s, pH 5,5												
Rejection	87,7	77,4	78,6	83,0	84,2	85,9	98,5	98,2	98,0	97,9	97,8	97,7
flux	1080	260	1370	1230	1260	1230	560	620	660	690	710	710

Table A19 Standardization test results (Fe-Cl₂ test run)

Module No.	Time After start (Mins)	Flow Direction	% Rejection			Flux (Corr) $\ell.m^{-2}.d^{-1}$		
			Before test	Fouled Condition (30 Hours)	Cleaned Condition (30 Hours)	Before test	Fouled Condition (30 Hours)	Cleaned Condition (30 Hours)
12	30	12 → 16	88,64	84,37	89,36	884	849	859
	60	"	88,96	83,93	88,90	876	845	885
	90	16 → 12	87,31	83,16	87,95	839	810	852
	120	"	88,23	83,39	87,66	830	826	866
16	30	12 → 16	75,02	56,57	75,99	1273	1185	1243
	60	"	74,92	56,37	75,54	1254	1135	1280
	90	16 → 12	77,70	61,37	78,72	1247	1115	1260
	120	"	78,73	61,53	78,03	1240	1159	1237

Table A20 Total Organic Carbon (TOC), Total Organohalogen precursors (TOHP) and UV 275 absorbance analyses

Date 1983	Raw Feed			Pretreated Feed		Bakke RO permeate			PCI RO		
	TOC mg/ℓ	TOHP μg/ℓ	UV Abs. 275 nm	TOC mg/ℓ	UV Abs. 275 nm	TOC mg/ℓ	TOHP μg/ℓ	UV Abs. 275 nm	TOC mg/ℓ	TOHP μg/ℓ	UV Abs. 275 nm
20/09	9,8	2642	0,275	5,8	0,142	0,8	5656	0,054	0,2	3832	-
27/09	11,0	1915	0,275	6,6	0,154	<1,0	1843	-	<1,0	1533	-
04/10	9,4	1533	0,237	5,8	0,100	1,0	1013	0,010	1,0	782	0,010
12/10	10,8	1634	-	-	-	3,8	1065	0,020	1,6	792	0,010
18/10	8,8	2105	0,239	5,4	0,144	1,0	2030	0,090	1,2	1585	0,010
01/11	16,0	1000	-	-	-	5,0	1000	0,080	3,2	1000	0,010
08/11	10,4	1736	0,290	5,8	0,139	1,8	2102	0,020	1,0	2504	0,010
22/11	9,8	> 1000	0,265	5,0	0,118	0,4	> 1000	0,030	0,6	> 1000	0,010
06/12	10,8	868	0,268	6,4	0,131	1,6	435	0,040	1,6	522	0,020
13/12	9,8	> 1000	0,268	6,2	0,137	<1,0	655	-	2,0	314	-

Table A21 Analyses of Samples - Bakke PO Unit

Date Sampled	28-06-1983				26-07-1983				23-08-1983				21-09-1983				
	Feed	Per-meate	Re-ject	% Re-jection	Feed	Per-meate	Re-ject	% Re-jection	Feed	Per-meate	Re-ject	% Re-jection	Feed	Per-meate	Re-ject	% Re-jection	
K	mg/ℓ	13,8	1,4	48,1	89,9	14,2	1,0	54	92,9	14,2	1,4	55,2	90,1	13,5	1,5	57	89,1
Na	mg/ℓ	32,7	13,5	280,6	83,7	94,6	11,5	329	37,8	96	15,2	177	54,2	116	16	188	34,2
Ca	mg/ℓ	51,4	1,4	186,9	97,28	53,7	1,0	200	98,1	50	2,0	193	36,0	46	1,4	147	87,1
Mg	mg/ℓ	8,5	0,28	31,3	96,71	9,5	0,24	35,6	97,5	8,5	0,4	34,1	35,3	0	<1,0	36	41,9
NH ₃ -N	mg/ℓ	0,2	<0,1	0,2	>50	<0,1	<0,1	<0,1	-	0,1	<0,1	0,2	-	0,2	<0,1	0,2	-
Fe	mg/ℓ					0,07	0,03	0,15	-	0,05	0,01	0,01	-	0,07	0,02	0,01	-
SO ₄	mg/ℓ	123	2	473	>98,27	140	2	528	98,6	133	2	550	98,5	140	<1	595	97,1
Cl	mg/ℓ	134	12,9	475	90,37	147	12	534	31,8	148	17	575	38,5	153	19	615	37,6
Alkalinity as CaCO ₃	mg/ℓ	17	<5	54	>70,59	17	2	54	88,2	14	4,5	47	67,9	18	<5	64	70,2
NO ₂ + NO ₃ - N	mg/ℓ	6,6	2,3	18,3	65,15	5,4	1,8	14,8	66,7	8,8	3,4	25,5	61,4	5,4	2,5	15,0	53,7
P (Reactive)	mg/ℓ	0,04	<0,03	0,11	-	<0,1	<0,1	<0,1	-	0,1	<0,1	0,2	-	0,1	<0,1	0,2	-
TDS (Calculated)	mg/ℓ	464	48	1642	90	504	39	1813	92,4	506	59	1955	39,4	514	57	2035	88,5
COD	mg/ℓ	40	0	68	100	24	4	64	83,3	28	3	109	71,4	20	0	100	100
TOC	mg/ℓ	5,0	0,6	14,0	88,0	6,0	0,8	12	86,7	7,4	0,8	11,6	89,2	5,8	0,8	20,4	86,2
Absorbance UV 275 nm		0,086	0,026	0,256	-	0,099	0,017	0,296	-	0,105	0,027	0,350	-	0,158	0,054	0,470	-
Absorbance (UV254-VIS545)		0,084	0,007	0,309	-	0,104	0,002	0,374	-	0,116	0,011	0,448	-	0,142	0,048	0,564	-
Conductivity	mS/m	80	7,8	260	90,25	90	8	290	31,11	88	11,2	305	37,3	89	11,5	325	37,1
pH		6,1	5,5	6,5	-	5,8	5,4	6,1	-	6,1	5,5	6,4	-	6,1	5,5	6,5	-

Date Sampled	29-09-1983				04-10-1983				18-10-1983				17-11-1983				
	Feed	Per-meate	Re-ject	% Re-jection	Feed	Per-meate	Re-ject	% Re-jection	Feed	Per-meate	Re-ject	% Re-jection	Feed	Per-meate	Re-ject	% Re-jection	
K	mg/ℓ	15,4	1,9	64	88,3	15,6	2,3	62	85,3	15,2	2,5	59,6	83,55	14,3	2,6	54,2	81,82
Na	mg/ℓ	47	17	382	82,5	89	20,0	339	77,5	81,0	16,1	293,5	80,12	94,8	21,1	337,0	77,74
Ca	mg/ℓ	67	2,1	202	96,9	48	2,9	204	94,0	45,1	2,0	186,0	95,57	38,8	1,7	148,0	95,82
Mg	mg/ℓ	8	0,3	37	96,7	9	0,5	41	94,4	9,0	0,37	37,6	95,89	5,5	0,37	22,2	93,27
NH ₃ -N	mg/ℓ	0,1	<0,1	0,2	-	0,1	<0,1	0,2	-	0,49	0,30	1,35	38,78	0,15	0,14	0,28	6,67
Fe	mg/ℓ	0,06	0,04	0,16	-	0,04	0,02	0,23	-	0,09	-	0,14		0,05	-	0,14	
SO ₄	mg/ℓ	116	2	517	98,3	92	2	440	97,8	92	2	417	97,83	115	2	485	98,26
Cl	mg/ℓ	158	21	624	86,7	149	21	618	85,9	140	18	552	87,14	147	33	514	77,55
Alkalinity as CaCO ₃	mg/ℓ	32	<5	55	>93,9	9	<5	29	>44,4	13	3	48	76,92	13	4	36	69,23
NO ₂ + NO ₃ - N	mg/ℓ	6,9	2,8	17,1	59,4	11,8	5,5	31,9	53,4	10	4,1	8,1	59,0	2,4	1,5	1,9	37,50
P (Reactive)	mg/ℓ	0,1	<0,1	0,2	-	0,1	<0,1	0,2	-	<0,1	<0,1	<0,1	-	<0,1	<0,1	<0,1	-
TDS (Calculated)	mg/ℓ	593	63	1970	39,4	466	80	1881	82,9	443	63	1642	35,69	442	72,8	1613	83,55
COD	mg/ℓ	22	4	92	81,8	22	4	60	81,8	16	4	83	75,0	28	8	83	71,4
TOC	mg/ℓ	6,6	<1	>20	>85	5,8	1,0	13,2	82,8	5,4	1,0	12,6	81,5	5,8	1,81	18,4	69,2
Absorbance UV 275 nm		0,136	0,055	0,403	-	0,104	0,060	0,272	-	0,141	0,063	0,417	-	0,129	0,060	0,334	-
Absorbance (UV254-VIS545)		0,133	0,033	0,496	-	0,099	0,029	0,338	-	0,123	0,016	0,474	-	0,110	0,019	0,354	-
Conductivity	mS/m	87,6	10,76	294,1	87,72	87,6	12,1	366,6	96,19	79,2	11,4	270,1	85,61	81,7	13,59	268,1	83,37
pH		5,9	5,5	6,3	-	6,0	5,5	6,5	-	5,95	5,45	6,35	-	6,0	5,5	6,3	-

ble A22 Analyses of Samples - PCI RO Unit

Date Sampled		28-06-1983				26-07-1983				23-08-1983				20-09-1983			
		Feed	Per-meate	Re-ject	% Re-jection	Feed	Per-meate	Re-ject	% Re-jection	Feed	Per-meate	Re-ject	% Re-jection	Feed	Per-meate	Re-ject	% Re-jection
a	mg/l	29,9	0,38	33,0	98,73	32,6	0,5	35,4	98,47	37,5	0,4	41,9	98,93	39	0,4	42	98,97
	mg/l	175,2	1,03	196,9	99,41	216,1	1,5	229,7	99,31	248	1,8	276	99,27	274	2	297	99,27
a	mg/l	113,3	<0,1	130,2	99,91	126,0	<0,1	136,0	99,92	133	0,3	143	99,77	132	<1	140	>99,24
g	mg/l	18,9	<0,1	21,1	99,47	22,1	<0,1	24,2	99,55	23,2	0,1	28,2	99,57	25	<1	26	>96,0
H ₃ -N	mg/l	0,2	<0,1	0,2	>50	<0,1	<0,1	<0,1		0,2	<0,1	0,2	>50	0,2	<0,1	0,2	>50,0
	mg/l					0,17	0,02	0,12		0,17	0,0	0,14					
O ₄	mg/l	292	<2	322	>99,32	326	1	342	99,69	375	1	407	99,73	408	<1	453	>99,75
	mg/l	294	<1	322	>99,66	368	1,5	379	99,59	395	1	425	99,75	426	2	448	99,53
alkalinity as CaCO ₃	mg/l	34	<5	39	>85,3	37	0	40	100	31	2,4	33	92,26	44	<5	47	>88,64
O ₂ + NO ₃ - N (Reactive)	mg/l	11,7	0,1	12,7	99,15	9,8	<0,2	10,0	97,96	18,3	0,1	20,7	99,45	12,4	0,1	12,5	99,19
	mg/l	0,25	<0,03	(0,04)	>88	<0,1	<0,1	<0,1	-	0,2	<0,1	0,2	>50	0,2	<0,1	0,2	>50
DS (Calculated)	mg/l	1018	11,4	1129	98,9	1180	6,0	1240	99,5	1331	8,4	1449	99,37	1414	<14,4	1519	>99,0
OD	mg/l	88	0	(36)	100	28	0	44	100	65	0	60	100	72	0	66	100
OC	mg/l	11,0	0,6	11,8	94,6	9,8	0	10,0	100	11,6	0,4	12,0	96,6	15,2	0,2	15,0	98,7
bsorbance UV 275 nm		0,163	0,026	0,169	-	0,161	0,013	0,170	-	0,282	0,015	0,268	-	0,329	0,065	0,354	-
bsorbance (UV254-VIS545)		0,186	0,003	0,194	-	0,192	0,014	0,201	-	0,350	0,021	0,336	-	0,414	0,020	0,446	-
onductivity	mS/m	160	0,86	190	99,46	190	1,05	205	99,5	220	1,4	240	99,4	233	1,5	253	99,4
i		6,4	5,4	6,4	-	6,1	5,6	6,1	-	6,4	5,8	6,4	-	6,5	5,8	6,5	-

Date Sampled		29-09-1983				04-10-1983				18-10-1983				17-11-1983			
		Feed	Per-meate	Re-ject	% Re-jection	Feed	Per-meate	Re-ject	% Re-jection	Feed	Per-meate	Re-ject	% Re-jection	Feed	Per-meate	Re-ject	% Re-jection
a	mg/l	45	0,5	51	98,89	46	0,5	52	98,91	42	0,4	44,7	99,05	52,3	0,4	57,9	99,24
	mg/l	281	2,3	321	99,18	261	3,0	286	98,85	188	2,4	227,4	98,72	325,4	2,9	366,0	99,11
a	mg/l	147	0,4	158	99,73	153	0,4	161	99,74	134	0,16	142,7	99,88	144,1	0,16	170,0	99,89
g	mg/l	26	0,1	30	99,62	31	0,2	33	99,35	26	0,05	28,9	99,81	20,5	0,05	24,4	99,76
H ₃ -N	mg/l	0,2	<0,1	0,2	>50	0,2	<0,1	0,2	>50	1,08	0,03	1,09	97,22	0,16	0,07	0,26	56,25
	mg/l	0,14	0,03	0,14	-	0,11	0,01	0,10		0,11	-	0,12	-	0,14	-	(0,30)	-
O ₄	mg/l	394	2	429	99,49	381	2	375	99,48	294	2	330	>99,32	452	2	520	99,56
	mg/l	455	2,3	491	99,49	461	3,0	515	99,35	386	2	415	99,48	482	4	586	99,17
alkalinity as CaCO ₃	mg/l	43	<5	51	>88,37	22	<5	23	>77,3	35	0	36	100,0	33	0	39	100,0
O ₂ + NO ₃ - N (Reactive)	mg/l	12,9	0,1	14,1	99,22	7,5	0,2	28,1	97,33	10,0	0,1	11,0	99,0	3,0	0,1	2,2	96,67
	mg/l	0,2	<0,1	0,2	>50	0,2	<0,1	0,2	>50	<0,1	<0,1	-	-	<0,1	<0,1	0,1	-
DS (Calculated)	mg/l	1458	14,57	1605	99,00	1394	16,5	1575	98,82	1159	7,80	1283	99,33	1530	10,34	1728	99,32
OD	mg/l	80	0	60	100	60	0	60	100	56	6	60	89,3	72	6	89	91,7
OC	mg/l	17,2	<1	18,2	>94	12,2	1,0	12,4	91,8	11,8	1,2	11,4	89,8	17,8	1,0	19,4	94,4
bsorbance UV 275 nm		0,286	0,057	0,308	-	0,225	0,052	0,247	-	0,300	0,059	0,325	-	0,291	0,056	0,323	-
bsorbance (UV254-VIS545)		0,342	0,026	0,374	-	0,260	0,028	0,286	-	0,323	0,017	0,356	-	0,330	0,011	0,373	-
onductivity	mS/m	208,1	1,97	222,7	99,05	221,9	2,34	239,8	98,95	200	1,7	215	99,2	250	2,5	280	99,0
i		6,3	5,7	6,2	-	6,4	5,8	6,4	-	6,3	5,9	6,3	-	6,5	5,8	6,5	-

Table A23 Microbiological Analyses

Date Sampled	12-07-1983			19-07-1983			26-07-1983			30-08-1983		
	Raw Feed	Bakke Perm	PCI Perm	Raw Feed	Bakke Perm	PCI Perm	Raw Feed	Bakke Perm	PCI Perm	Raw Feed	Bakke Perm	PCI Perm
Standard Plate Count (per 1 mL)	38×10^2	5	45	61×10^2	6	12	20×10^3	8	20	20×10^4	16	1
Total Coliforms (per 100 mL)	317	0	0	223	0	0	170	0	0	320	0	0
Faecal Coliforms (per 100 mL)	9	0	0	4	0	0	8	0	0	4	0	1
Faecal Streptococci (per 100 mL)	1	0	0	0	0	0	1	0	0	1	0	0
Enteric Viruses (per 10 L)	155	0	0	116	0	0	0	0	0	0	0	0
Coliphages (per 10 mL)	2	0	0	2	0	0	10	0	0	3	0	0

Date Sampled	23-08-1983			06-09-1983			20-09-1983			27-09-1983		
	Raw Feed	Bakke Perm	PCI Perm	Raw Feed	Bakke Perm	PCI Perm	Raw Feed	Bakke Perm	PCI Perm	Raw Feed	Bakke Perm	PCI Perm
Standard Plate Count (per 1 mL)	90×10^2	32	9	81×10^2	9	123	81×10^2	14	7	32×10^3	17	167
Total Coliforms (per 100 mL)	367	0	0	380	0	0	217	0	0	293	0	0
Faecal Coliforms (per 100 mL)	111	0	0	4	0	0	4	0	0	7	0	0
Faecal Streptococci (per 100 mL)	0,3	0	0	0	0	0	0	0	0	1	0	0
Enteric Viruses (per 10 L)	0	0	0	0	0	0	92	0	0	92	0	0
Coliphages (per 10 mL)	3	0	0	NR	0	0	2	0	0	25	0	1

Table A24 Microbiological Analyses (Pretoria Laboratory)

Date Sampled	04-10-1983			18-10-1983			01-11-83			08-11-1983		
	Raw Feed	Bakke Perm	PCI Perm	Raw Feed	Bakke Perm	PCI Perm	Raw Feed	Bakke Perm	PCI Perm	Raw Feed	Bakke Perm	PCI Perm
Standard Plate Count (per 1 mL)	42x10 ³	377	307	93x10 ³	8	643	19x10 ³	248	227	94x10 ²	1	68
Total Coliforms (per 100 mL)	373	0	0	17	0	0	0G	138	137	250	0	0
Faecal Coliforms (per 100 mL)	9	0	0	2	0	0	206	0	0	8	0	0
Faecal Streptococci (per 100 mL)	2	0	0	2	0	0	0G	0	0	6	0	0
Enteric Viruses (per 10 L)	92	0	0	628	0	0	632	0	0	92	0	0
Coliphages (per 10 mL)	1	0	0	0	0	0	61	0	0	10	0	0

Date Sampled	22-11-1983			06-12-1983			13-12-1983		
	Raw Feed	Bakke Perm	PCI Perm	Raw Feed	Bakke Perm	PCI Perm	Raw Feed	Bakke Perm	PCI Perm
Standard Plate Count (per 1 mL)	12x10 ³	120	170	52x10 ³	20	36	14x10 ⁴	290	46
Total Coliforms (per 100 mL)	607	0	0	1570	0	0	470	0	0
Faecal Coliforms (per 100 mL)	26	0	0	16	0	0	15	0	0
Faecal Streptococci (per 100 mL)	1	0	0	3	0	0	3	0	0
Enteric Viruses (per 10 L)	0	0	0	632	0	0	ND	ND	ND
Coliphages (per 10 mL)	4	0	0	9	0	0	ND	ND	ND

Table A25 AMES TESTS FOR MUTAGENICITY

Date of Sampling	Salmonella Typh. Strain	TA 98						TA 100					
		With			Without			With			Without		
		MR	N	$\frac{A}{\text{Plate}}$	MR	N	$\frac{A}{\text{Plate}}$	MR	N	$\frac{A}{\text{Plate}}$	MR	N	$\frac{A}{\text{Plate}}$
20/09/83	Raw Feed PCI Permeate	4,7 2,5	3 3	2,7 2,7	2,5 4,0	3 3	2,7 2,7	1,5 1,1	3 2	2,7 2,7	T 1,5	3 1	2,7 2,7
29/09/83	Raw Feed PCI Permeate	T 1,9	3 3	2,7 2,7	T 1,1	3 3	2,7 2,7	T 1,1	3 3	2,7 2,7	T 0,9	3 3	2,7 2,7
18/10/83	Raw Feed PCI Permeate	T 1,3	3 3	2,7 2,7	T 1,0	3 3	2,7 2,7	T T?	3 3	2,7 2,7	T T?	3 3	2,7 2,7
08/11/83	Raw Feed PCI Permeate	5,8 1,4	3 3	2,7 2,7	1,2 1,3	3 3	2,7 2,7	1,9 1,9	3 3	2,7 2,7	0,5 1,2	3 3	2,7 2,7

MR = Mutation Ratio = $\frac{\text{Number of revertants on test plate}}{\text{Number of revertants on control plate}}$

N = Number of tests on sample

$\frac{A}{\text{Plate}}$ = Average of $\frac{\text{Amount of original sample per test plate}}{\text{Number of revertants on control plate}}$

T = Toxic

? = Results uncertain

MR>2 = Indicates that mutagenicity is present

Table A26 Results from Port Elizabeth Study (Vail and Barnard, 1986)

CHEMICAL RESULTS COMPOSITE DAILY SAMPLES											
Results in mg/l unless otherwise stated	Feed			Product					% Rejection		
	n	M	SD	n	M	95% CI		SD	n	M	SD
						H	L				
Conductivity, mS/m	259	129	21	259	14,5	22	7,1	3,8	259	89	2,0
Sodium (as Na)	35	266	58	35	30,5	48	12	9,1	35	89	1,9
Potassium (as K)	35	30	2,6	35	3,2	5,1	1,3	0,98	35	89	3,2
Calcium (as CaCO ₃)	60	86	14	60	4,7	11	Nil	3,25	60	95	3,4
Magnesium (as CaCO ₃)	58	74	20	58	5,4	16	Nil	5,4	58	93	6,3
Total alkalinity (as CaCO ₃)	60	120	33	60	7,8	12	3,2	2,35	60	93	3,2
Chloride (as Cl ⁻)	34	318	82	34	39	67	11	14	34	88	2,1
Sulphate (as SO ₄)	35	93**	24	34	3,8	6,9	0,7	1,6	34	96*	1,8*
Total phosphorus (as P)	35	3,4	1,85	35	0,09	0,19	Nil	0,05	35	97	1,8
Silica (as SiO ₂)	35	11	1,2	35	2,0	2,9	1,1	0,45	35	82	4,1
Ammonia (as N)	58	10	4,5	58	1,7	3,2	0,2	0,78	58	82	6,3
Nitrite (as N)	56	0,13	0,14	56	0,01	(0,19)	(<0,01)	NA	ND	ND	ND
Nitrate (as N)	54	4,8	4,5	54	2,1	5,8	Nil	1,9	54	53	13
Colour (Hazen units)	60	30	12	60	<5	(<5)	(<5)	NA	ND	ND	ND
Turbidity (NTU)	60	2,4	1,3	60	0,40	0,67	0,13	0,14	60	82	7,3
Absorbance (275 nm)	75	0,27	0,05	57	0,013	0,031	Nil	0,009	57	95	2,9
Abs. (254-545 nm)	54	0,35	0,05	54	0,020	0,04	Nil	0,01	54	95	3,2
COD	37	55	8,1	37	6,3	13,5	Nil	3,7	37	89	6,7
Suspended solids	39	3,5	2,3	Nil	ND	ND	ND	ND	Nil	ND	ND
pH (laboratory)	Nil	ND	ND	58	5,4	(6,1)	(4,4)	NA	NA	ND	ND
pH (machine)*	220	6,0	NA	Nil	ND	ND	ND	ND	NA	ND	ND
Free residual chlorine (Cl ₂)	214	0,1	NA	Nil	ND	ND	ND	ND	Nil	ND	ND
Total residual chlorine (Cl ₂)	42	0,7	NA	Nil	ND	ND	ND	ND	Nil	ND	ND

n = number of samples M = mean or median SD = standard deviation 95% CI = 95% confidence limits; H = higher limit, L = lower limit
 (X) - maximum and minimum results ND - not determined
 * - after addition of sulphuric acid NA - not applicable
 ** - before addition of sulphuric acid < - less than
 • - uncorrected for sulphuric acid addition

Table A27 Results from Port Elizabeth Study (Vail and Barnard, 1986)

MICRO-POLLUTANTS COMPOSITE DAILY SAMPLES											
Results in $\mu\text{g}/\ell$	Feed			Product					% Rejection		
	n	M	SD	n	M	95% CL		SD	n	M	SD
						H	L				
Aluminium	32	14	5.9	Nil	ND	ND	ND	ND	Nil	ND	ND
Arsenic	32	<0.2	NA	Nil	ND	ND	ND	ND	Nil	ND	ND
Cadmium	35	<0.3	NA	35	<0.2	(<0.2)	(<0.2)	NA	NA	NA	NA
Chromium (total)	35	7.0	NA	35	<2.5	(10)	(<2.5)	NA	35	>69	NA
Copper	30	5.0	1.6	30	0.8	(2.0)	(<0.8)	NA	30	82	NA
Iron	35	129	151	35	10.0	27	Nil	8.7	35	89	9.7
Lead	35	<5	NA	35	<2.5	(<2.5)	(<2.5)	NA	NA	NA	NA
Manganese	35	44	17	31	2.1	3.7	0.55	0.79	31	95	4.2
Mercury	35	<0.5	NA	Nil	ND	ND	ND	ND	Nil	ND	ND
Molybdenum	35	<24	NA	35	<12	(<12)	(<12)	NA	NA	NA	NA
Nickel	35	21	9.0	35	<0.8	(4.0)	(<0.8)	NA	35	>95	NA
Selenium	35	<0.4	NA	Nil	ND	ND	ND	ND	Nil	ND	ND
Zinc	35	72	19	35	7.8	15	0.94	3.5	35	89	5.4
Boron (B)	35	234	33	Nil	ND	ND	ND	ND	Nil	ND	ND
Cyanide (CN)	34	17	15	17	4.9	11	Nil	3.1	17	50	28
Detergents (as MBAS)	34	196	74	31	11	28	Nil	8.7	31	95	3.2
Fluoride (F)	35	100	141	Nil	ND	ND	ND	ND	Nil	ND	ND
Chloroform	42	21	15	42	20	49	Nil	15	ND	ND	ND
Bromodichloromethane	42	20.5	14	42	21	48	Nil	13.6	ND	ND	ND
Dibromochloromethane	42	16	17.5	42	16	48	Nil	16.6	ND	ND	ND
Bromoform	40	8.5	22	39	8.0	42	Nil	17.6	ND	ND	ND

n = number of samples M = mean or median SD = standard deviation 95% CL = 95% confidence limits; H = higher limit, L = lower limit
(X) - maximum and minimum results ND - not determined NA - not applicable < - less than > - greater than

Table A28 Results from Port Elizabeth Study (Vail and Barnard, 1986)

BACTERIOLOGICAL RESULTS - SNAP SAMPLES

(i) Free residual chlorine in feed: Less than 0.2 mg/l

	Total Plate Count/ml				Total Coliforms/100 ml				E. Coli l/100 ml				Aerobic bacterial spores/100 ml			
	n	Max.	Min.	Med.	n	Max.	Min.	Med.	n	Max.	Min.	Med.	n	Max.	Min.	Med.
Feed	54	2 000 000	10	9 400	45	>200 000	0	60	44	>200 000	0	0	58	8 500	40	335
Product	58	8 600	0	200	61	5 800	0	1	47	1 060	0	0	61	90	0	6

(ii) Free residual chlorine in feed: 0.2 mg/l - 0.9 mg/l (median 0.3 mg/l)

	Total Plate Count/ml				Total Coliforms/100 ml				E. Coli l/100 ml				Aerobic bacterial spores/100 ml			
	n	Max.	Min.	Med.	n	Max.	Min.	Med.	n	Max.	Min.	Med.	n	Max.	Min.	Med.
Feed	39	7 200	0	160	42	2 100	0	0	38	37	0	0	44	4 700	0	190
Product	39	30	0	5	42	8	0	0	35	0	0	0	41	290	0	4

> = greater than

n = number of samples

max. = maximum

min. = minimum

med. = median value

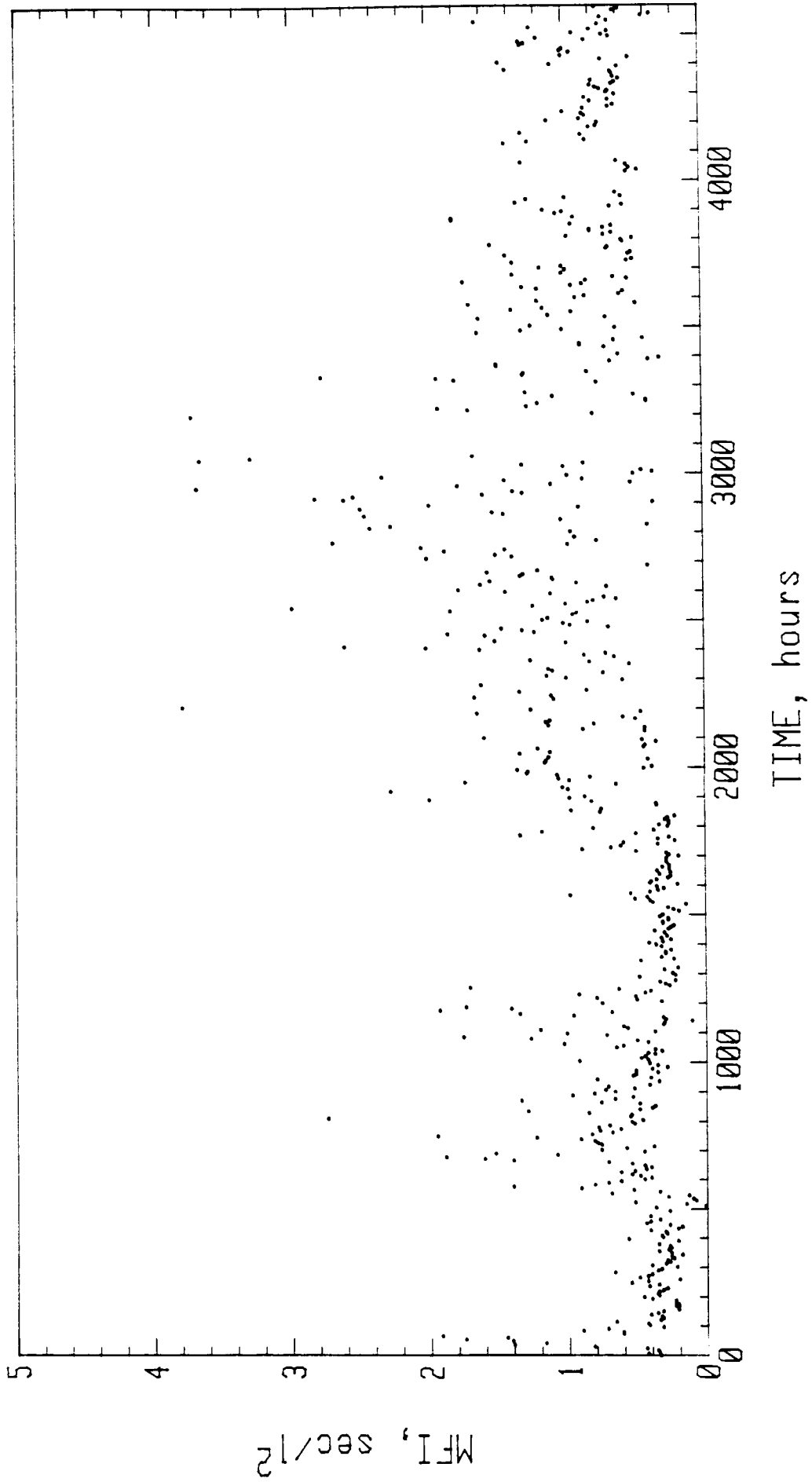


FIGURE A1 PRETREATMENT PLANT - MFI ON MULTI MEDIA FILTER EFFLUENT

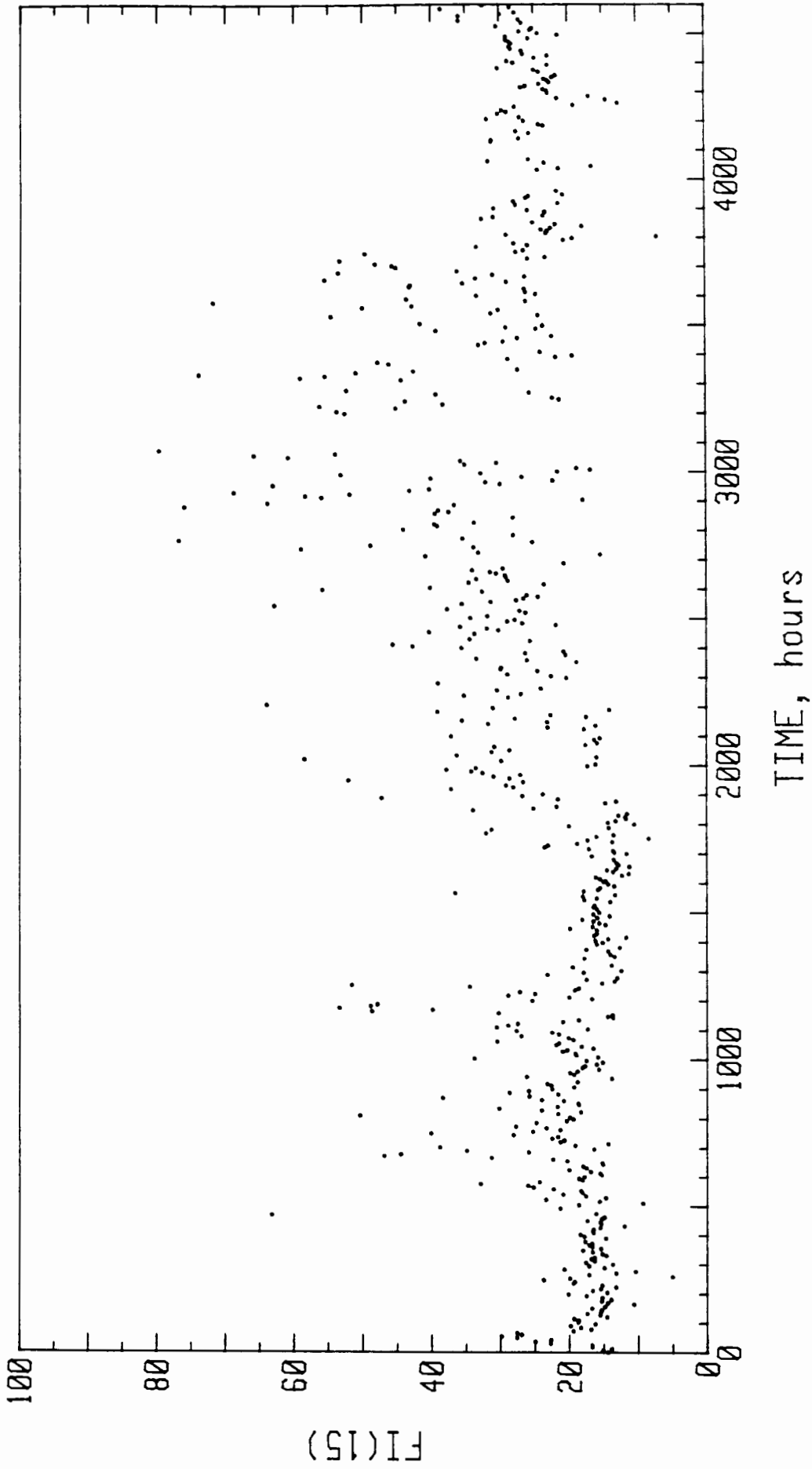


FIGURE A2 PRETREATMENT PLANT - FI(15) ON MULTI MEDIA FILTER EFFLUENT

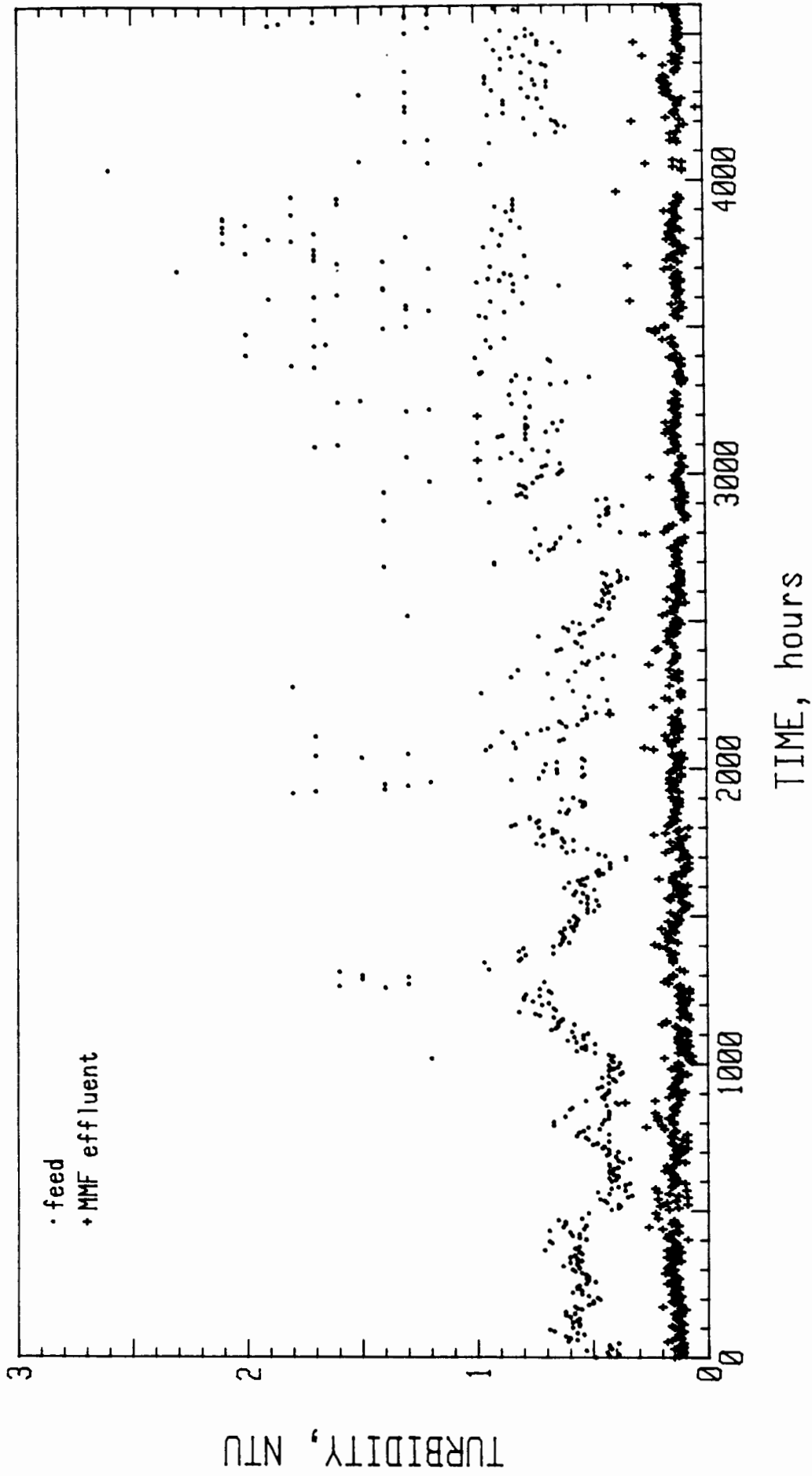


FIGURE A3 PRETREATMENT PLANT - TURBIDITY ON RAW FEED AND MMF EFFLUENT

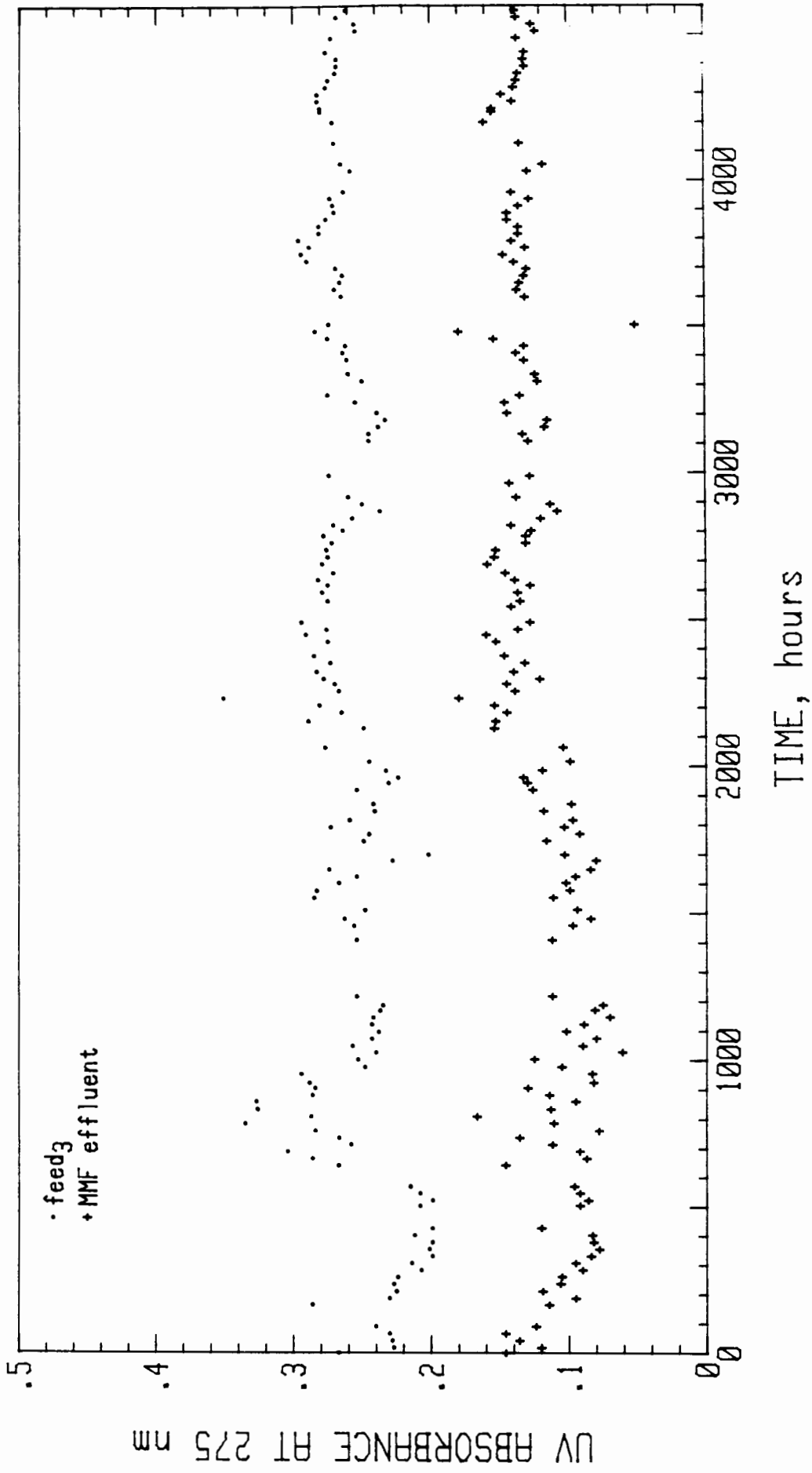


FIGURE A4 PRETREATMENT PLANT - UV ABSORBANCE AT 275 nm FOR RAW FEED AND MMF EFFLUENT

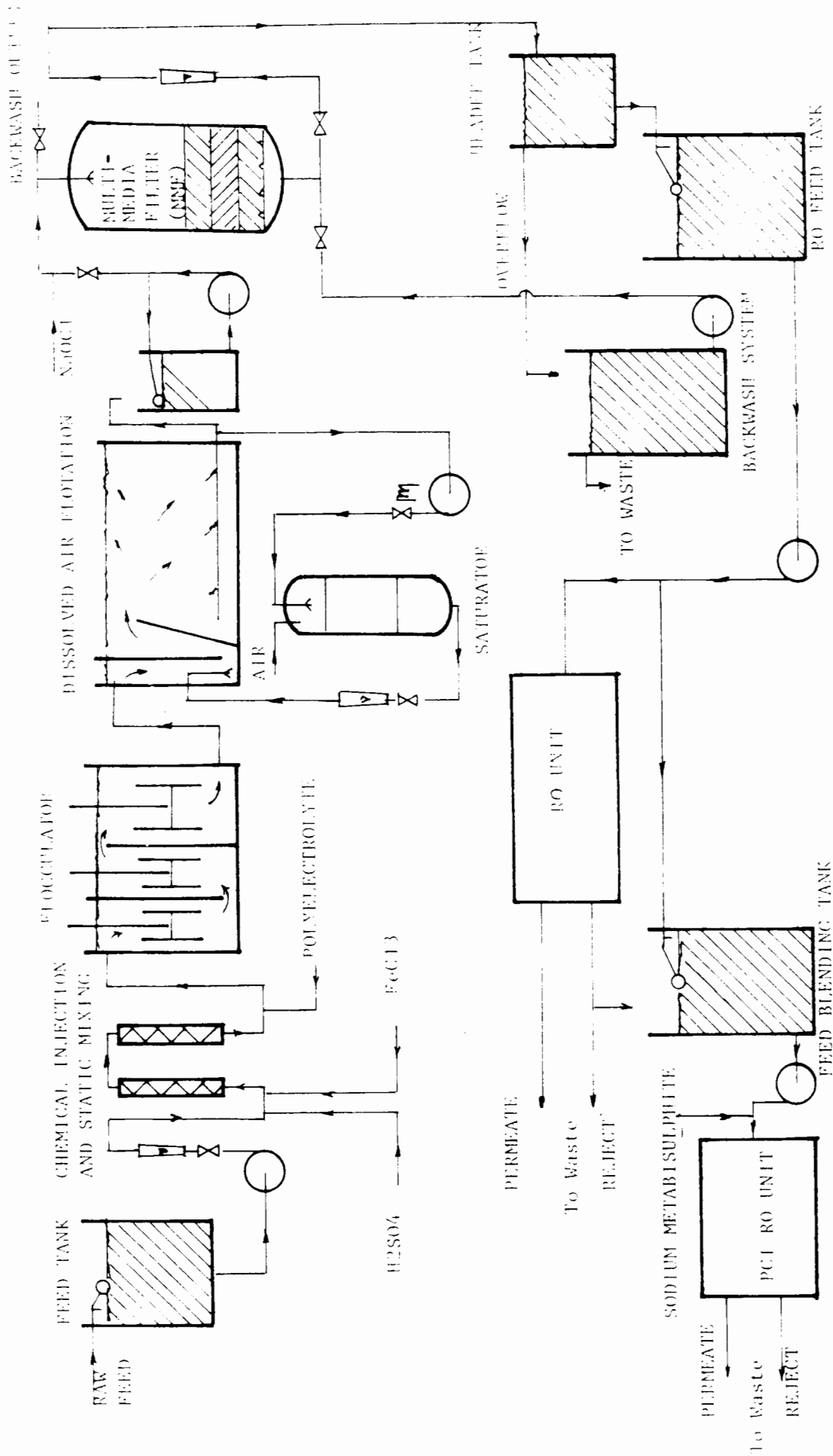


FIGURE A5 FLOWSHEET OF PILOT-SCALE RECLAMATION PLANT.

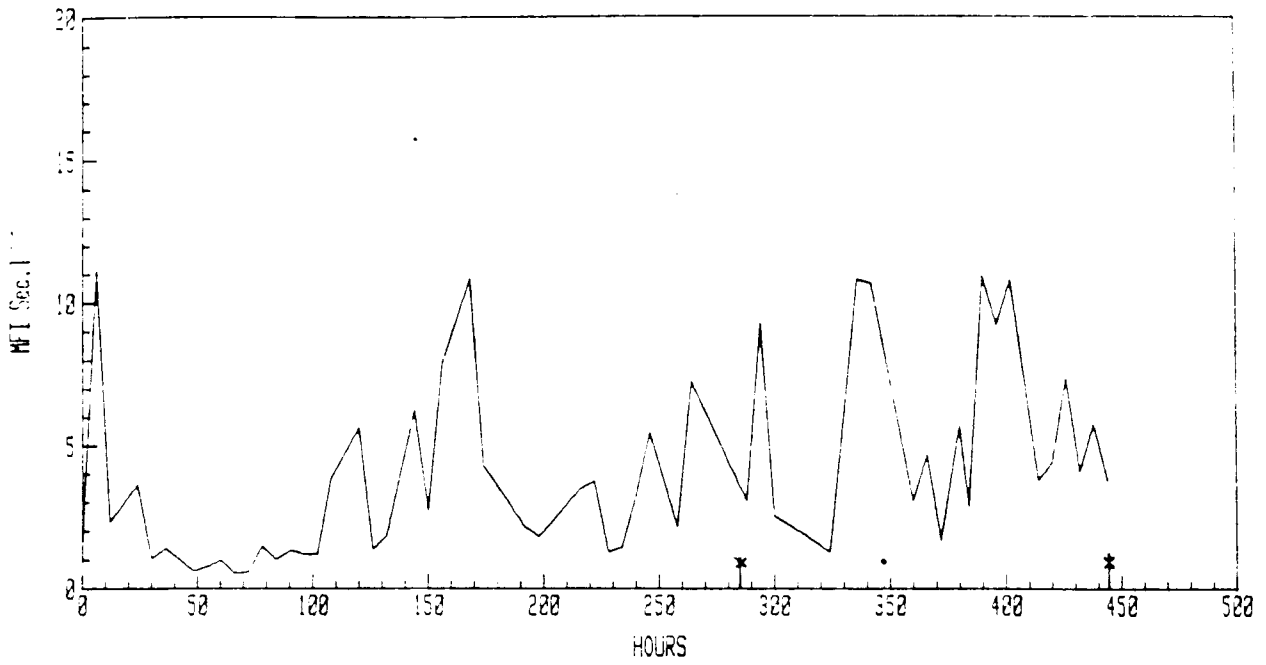


FIGURE A6 :MFI ON 3μ FILTERED DAF EFFLUENT(Fe and C573 Poly)

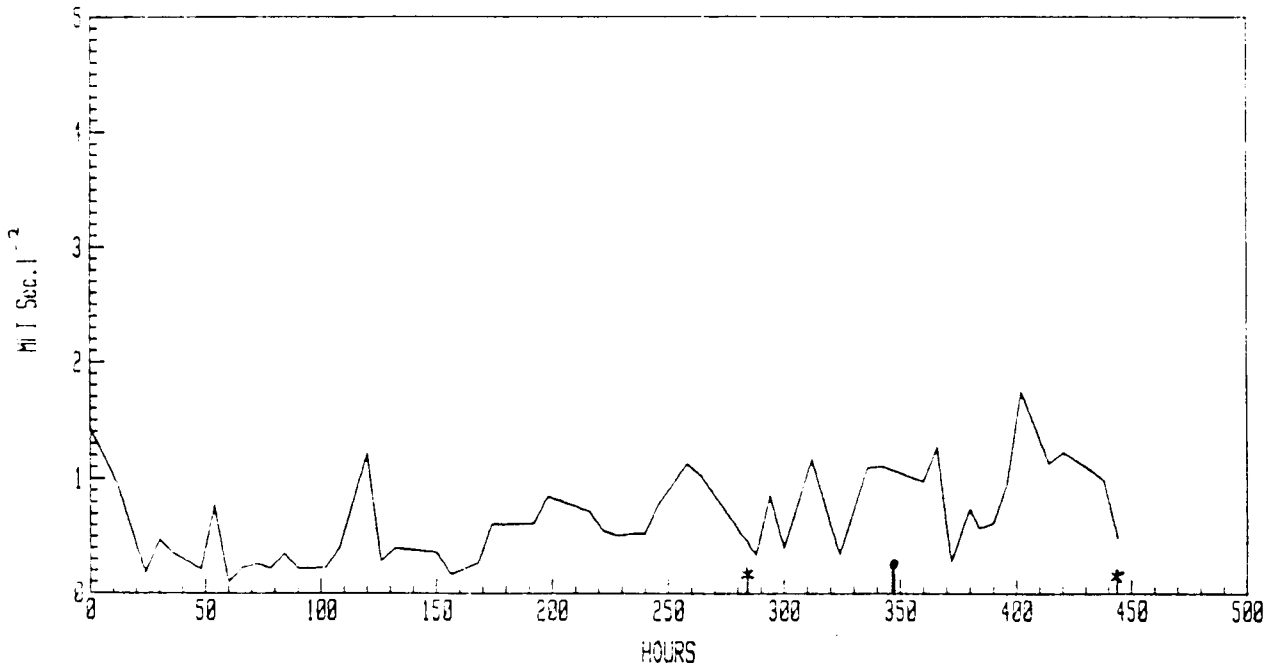


FIGURE A7 :MFI ON MMF EFFLUENT (Fe and C573 Poly)

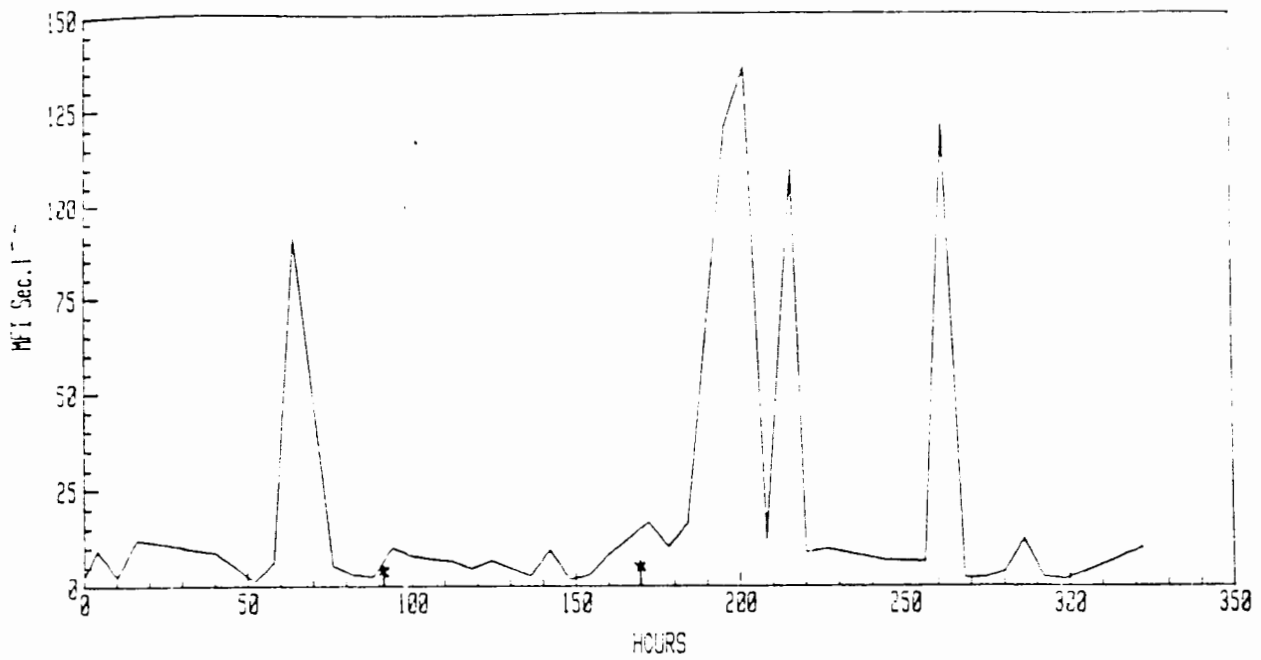


FIGURE A8 MFI ON 3μ FILTERED DAF EFFLUENT (Fe ONLY)

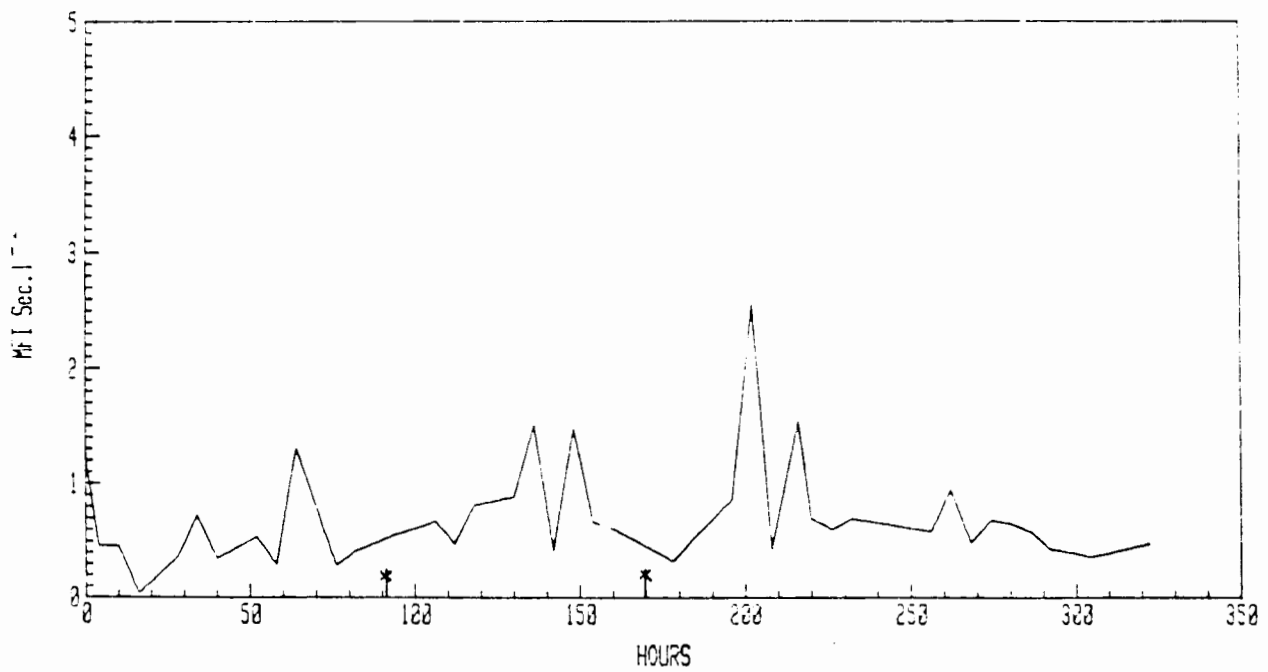


FIGURE A9 MFI ON MMF EFFLUENT (Fe ONLY)

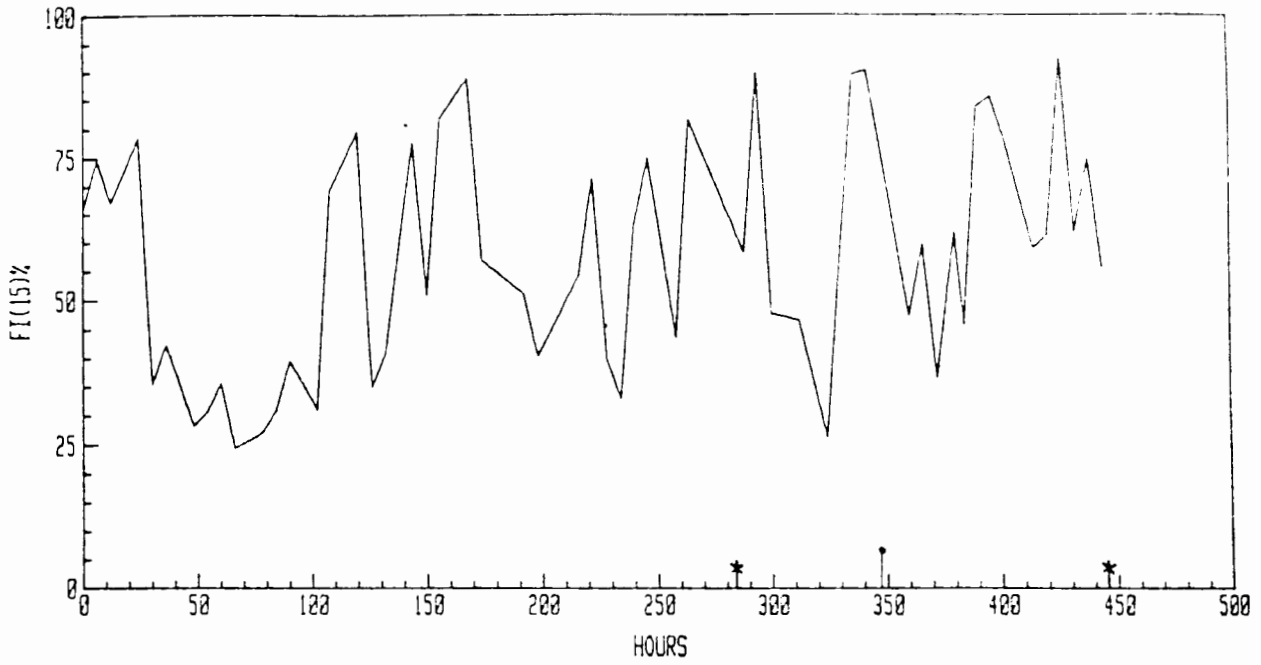


FIGURE A10 FOULING INDEX % ON 3µ FILTERED DAF EFFLUENT (Fe and C573 Poly)

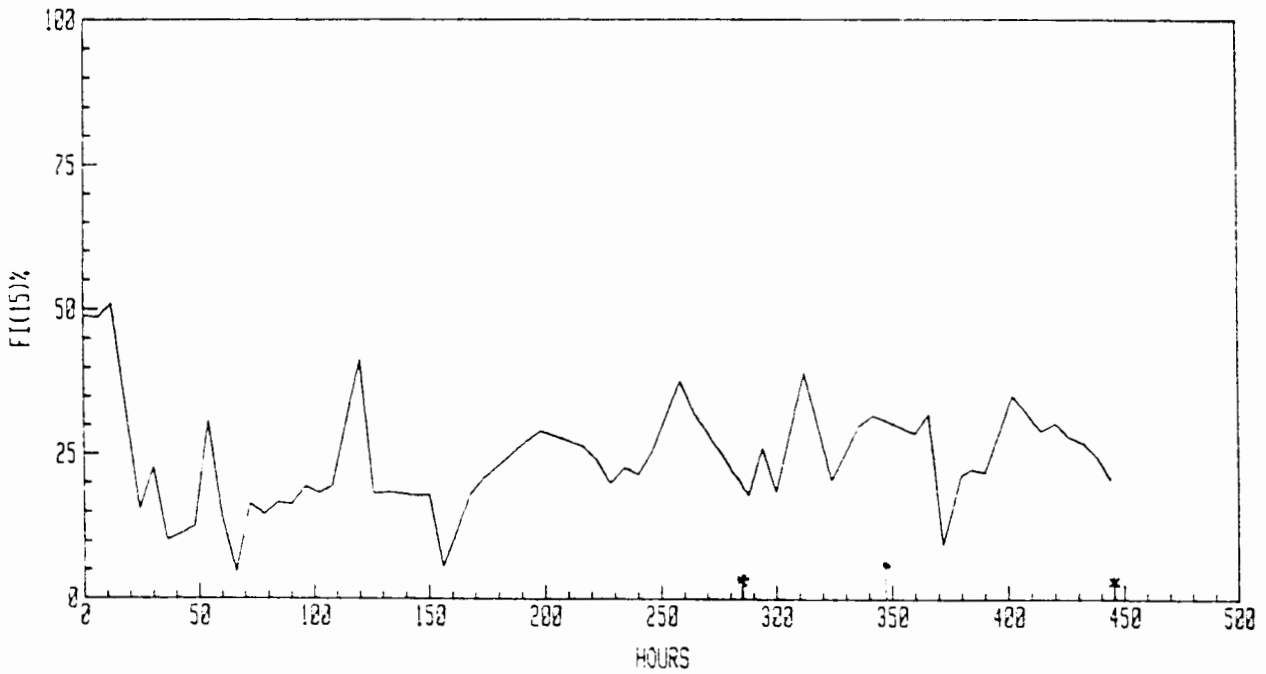


FIGURE A11 FOULING INDEX % ON MMF EFFLUENT (Fe and C573 Poly)

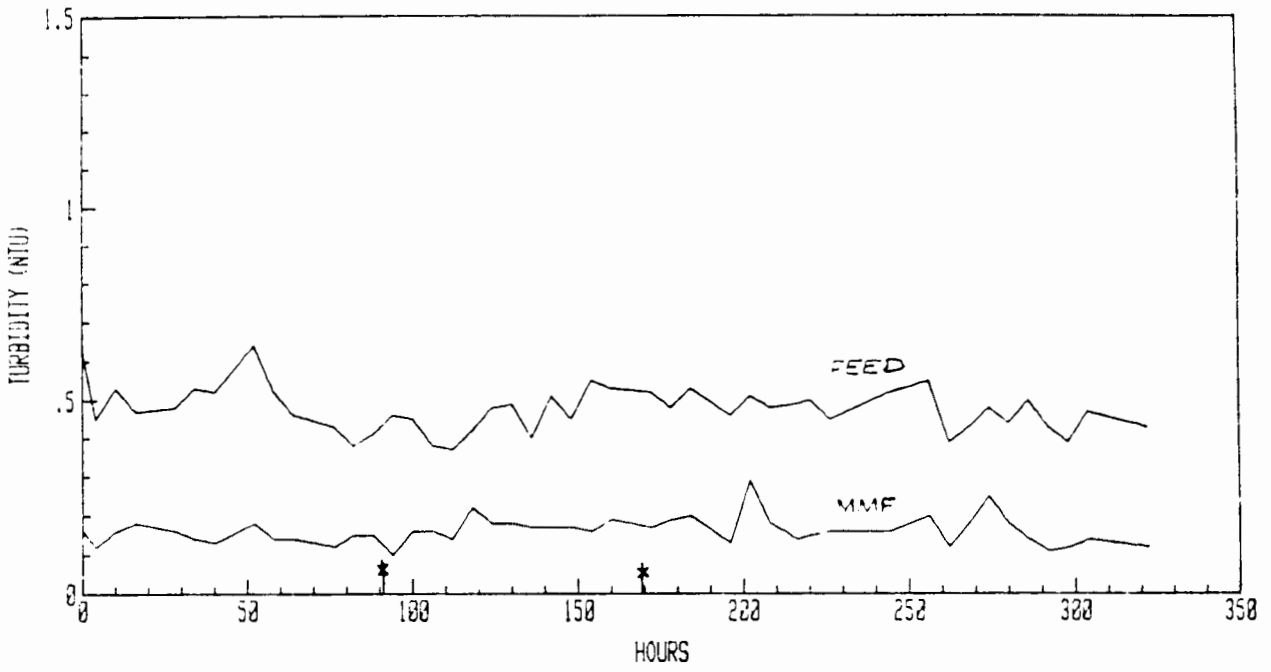


FIGURE A12 TURBIDITY OF FEED WATER AND MMF EFFLUENT (Fe ONLY)

APPENDIX BREVERSE OSMOSIS DATA ON ALKYL ALCOHOLS AND
ALKYL PHENOLS

TABLE B1	METHANOL
TABLE B2	ETHANOL
TABLE B3	1-PROPANOL
TABLE B4	2-PROPANOL
TABLE B5	1-BUTANOL
TABLE B6	2-BUTANOL
TABLE B7	2-METHYL 1-PROPANOL
TABLE B8	2-METHYL 2-PROPANOL
TABLE B9	1-PENTANOL
TABLE B10	1-HEXANOL
TABLE B11	1-HEPTANOL
TABLE B12	PHENOL
TABLE B13	4-METHYL PHENOL
TABLE B14	4-ETHYL PHENOL
TABLE B15	2,6-DIMETHYL PHENOL
TABLE B16	4-n-PROPYL PHENOL
TABLE B17	4-ISOPROPYL PHENOL

TABLE B1

METHANOL REVERSE OSMOSIS DATA

FT-30 membrane :

$$C_{f1} = 88,6 \text{ mg}/\ell = 2,77 \text{ mmol}/\ell \text{ methanol}$$

Col. (1)	(2)	(3)	(4)	(5)	(6)
RO Test cell	Permeate flux ml/15 min	$J_v \times 10^{-4}$ cm/s	$J_s \times 10^{-7}$ mmol/cm ² .s	C_p mmol/ℓ	Rejection
ΔP	5620 kPa (800 psi)				
A	60,2	36,9	63,5	1,72	0,38
B*	59,9	36,7	67,5	1,84	0,34
C	62,3	38,2	68,0	1,78	0,36
D	55,6	34,1	62,7	1,84	0,34
ΔP	2810 kPa (400 psi)				
A	31,3	19,2	40,3	2,1	0,24
B	29,4	18,0	37,6	2,09	0,25
C	31,8	19,5	38,8	1,99	0,28
D	29,0	17,8	35,1	1,97	0,27
ΔP	1405 kPa (200 psi)				
A	14,5	8,9	19,5	2,19	0,21
B	15,5	9,5	20,4	2,15	0,22
C	15,5	9,5	20,4	2,15	0,22
D	14,4	8,8	19,4	2,20	0,21

*Note : Test cell B was slightly bigger than the other cells 48,8 mm diameter compared to 48 mm giving a 6% larger surface area. All the data for cell B were, therefore, corrected by 6%.

FT-30 membrane :

$C_{f2} = 6,25 \text{ mmol}/\ell$ (200 mg/ ℓ) methanol

(1)	(2)	(3)	(4)	(5)	(6)
ΔP	5620 kPa				
A	58,1	35,6	140,3	3,94	0,37
B*	58,9	36,1	145,8	4,04	0,35
C	60,7	37,2	148,4	3,99	0,36
D	59,5	36,5	146,7	4,02	0,36
ΔP	2810 kPa				
A	29,7	18,2	82,6	4,54	0,27
B	29,4	18,0	81,0	4,5	0,28
C	31,2	19,1	84,2	4,41	0,29
D	29,0	17,8	80,3	4,51	0,28
ΔP	1405 kPa				
A	14,8	9,1	44,5	4,89	0,22
B	14,8	9,1	45,0	4,94	0,21
C	15,0	9,2	45,2	4,91	0,22
D	14,5	8,9	43,1	4,84	0,23

TABLE B2

ETHANOL REVERSE OSMOSIS DATA

FT-30 membrane :

 $C_{f1} = 2,47 \text{ mmol/l}; 114 \text{ mg/l ethanol}$

(1)	(2)	(3)	(4)	(5)	(6)
ΔP	5620 kPa				
A	63,0	38,6	23,9	0,62	0,75
B	64,8	39,7	25,8	0,65	0,74
C	60,2	36,9	23,6	0,64	0,74
D	63,9	39,2	23,5	0,60	0,76
ΔP	2810 kPa				
A	29,9	18,3	15,6	0,85	0,66
B	31,0	19,0	16,9	0,89	0,64
C	28,7	17,6	15,8	0,90	0,64
D	30,8	18,9	15,9	0,84	0,66
ΔP	1405 kPa				
A	14,8	9,1	10,4	1,14	0,54
B	15,3	9,4	10,9	1,16	0,53
C	14,5	8,9	10,0	1,12	0,55
D	15,0	9,2	10,1	1,10	0,55

FT-30 membrane :

 $C_f = 6,62 \text{ mmol/l}; 305 \text{ mg/l, ethanol}$

(1)	(2)	(3)	(4)	(5)	(6)
ΔP	= 5620 kPa				
A	60,5	37,1	66,0	1,78	0,73
B	61,2	37,5	64,5	1,72	0,74
C	60,2	36,9	66,4	1,80	0,73
D	62,3	38,2	70,3	1,84	0,72

ΔP	=	2810 kPa				
A		30,0	18,4	45,6	2,48	0,63
B		30,2	18,5	45,1	2,44	0,63
C		27,6	16,9	42,4	2,51	0,62
D		30,5	18,7	46,9	2,51	0,62
ΔP	=	1405 kPa				
A		14,7	9,0	27,0	3,00	0,55
B		14,7	9,0	27,5	3,05	0,54
C		14,4	8,8	26,8	3,05	0,54
D		14,5	8,9	27,9	3,13	0,53

FT-30 membrane :

$C_f = 16,92 \text{ mmol/l}; 780 \text{ mg/l, ethanol}$

(1)	(2)	(3)	(4)	(5)	(6)	
ΔP	=	5620 kPa				
A		58,4	35,8	163,2	4,56	0,73
B		59,5	36,5	166,4	4,56	0,73
C		56,8	34,8	153,1	4,40	0,74
D		57,4	35,2	154,9	4,40	0,74
ΔP	=	2810 kPa				
A		28,5	17,5	112,5	6,43	0,62
B		29,7	18,2	113,9	6,26	0,63
C		27,4	16,8	105,2	6,26	0,63
D		28,4	17,4	106,0	6,09	0,64
ΔP	=	1405 kPa				
A		12,2	7,5	58,4	7,78	0,54
B		13,2	8,1	64,4	7,95	0,53
C		11,7	7,2	57,2	7,95	0,53
D		12,1	7,4	56,3	7,61	0,55

SEPA-99 membrane (Permeate flux in $\text{m}\ell/45 \text{ min}$) :

$C_f = 16,9 \text{ mmol}/\ell$; $780 \text{ mg}/\ell$, ethanol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P = 5620 \text{ kPa}$					
A	29,4	6,0	76,8	12,8	0,24
B	31,3	6,4	78,7	12,3	0,27
C	29,8	6,1	71,4	11,7	0,31
D	28,4	5,8	72,5	12,5	0,26
$\Delta P = 2810 \text{ kPa}$					
A	14,7	3,0	39,0	13,0	0,23
B	15,2	3,1	39,7	12,8	0,24
C	14,2	2,9	36,3	12,5	0,26
D	13,7	2,8	35,8	12,8	0,24
$\Delta P = 1405 \text{ kPa}$					
A	12,2	6,9	18,2	13,0	0,23
B	13,2	7,3	19,5	13,0	0,23
C	11,7	6,8	17,2	12,3	0,27
D	12,1	6,9	18,2	13,0	0,23

TABLE B3

FT-30 membrane :

 $C_f = 4,28 \text{ mmol/l}$; mg/l , 1-propanol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa				
A	60,0	36,8	15,8	0,43	0,90
B	61,7	37,8	16,6	0,44	0,90
C	60,7	37,2	14,1	0,38	0,91
D	58,9	36,1	17,0	0,47	0,89
$\Delta P =$	4216 kPa				
A	44,2	27,1	11,9	0,44	0,90
B	48,8	29,9	13,2	0,44	0,90
C	46,5	28,5	13,4	0,47	0,89
D	43,4	26,6	13,0	0,49	0,88
$\Delta P =$	2810 kPa				
A	30,0	18,4	11,0	0,60	0,86
B	32,1	19,7	11,0	0,56	0,87
C	31,2	19,1	10,5	0,55	0,87
D	29,5	18,1	10,0	0,55	0,87
$\Delta P =$	1967 kPa				
A	21,4	13,1	8,9	0,68	0,84
B	22,0	13,5	9,3	0,69	0,84
C	21,9	13,4	8,8	0,66	0,85
D	21,0	12,9	9,4	0,73	0,83
$\Delta P =$	1300 kPa				
A	13,7	8,4	6,5	0,77	0,82
B	14,5	8,9	6,5	0,73	0,83
C	14,0	8,6	6,5	0,76	0,82
D	13,4	8,2	6,3	0,77	0,82

TABLE B4

FT-30 membrane :

 $C_f = 1,65 \text{ mmol/l}$; mg/l , 2-propanol

(*)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa				
A	63,8	39,1	3,1	0,08	0,95
B	62,6	38,4	1,9	0,05	0,97
C	61,8	37,9	2,7	0,07	0,96
D	60,7	37,2	2,6	0,07	0,96
$\Delta P =$	2810 kPa				
A	32,1	19,7	2,0	0,10	0,94
B	31,3	19,2	1,7	0,09	0,95
C	29,7	18,2	1,3	0,07	0,96
D	29,9	18,3	1,6	0,09	0,95
$\Delta P =$	1405 kPa				
A	16,5	10,1	1,3	0,13	0,92
B	16,5	10,1	1,2	0,12	0,93
C	15,8	9,7	1,0	0,10	0,94
D	16,0	9,8	1,0	0,10	0,94

FT-30 membrane :

 $C_f = 3,79 \text{ mmol/l}$; mg/l , 2-propanol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa				
A	63,8	39,1	4,3	0,11	0,97
B	63,6	39,0	3,1	0,08	0,98
C	61,0	37,4	4,5	0,12	0,97
D	61,2	37,5	5,6	0,15	0,96

$\Delta P = 2810$ kPa

A	31,8	19,5	3,7	0,19	0,95
B	32,1	19,7	3,0	0,15	0,96
C	31,2	19,1	4,4	0,23	0,94
D	30,5	18,7	3,7	0,20	0,95

$\Delta P = 1405$ kPa

A	16,1	9,9	2,6	0,26	0,93
B	15,8	9,7	2,2	0,23	0,94
C	15,8	9,7	2,6	0,27	0,93
D	15,3	9,4	2,3	0,24	0,94

FT-30 membrane :

$C_f = 15,0$ mmol/l; mg/l, 2-propanol

	(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P = 5620$ kPa						
A	61,0		37,4	16,8	0,45	0,97
B	61,3		37,6	17,3	0,46	0,97
C	57,4		35,2	10,6	0,30	0,98
D	58,6		35,9	21,5	0,60	0,96

ΔP	=	2810 kPa				
A		30,3	18,6	11,3	0,61	0,96
B		30,5	18,7	11,0	0,59	0,96
C		27,9	17,1	10,3	0,60	0,96
D		28,4	17,7	13,1	0,75	0,95
ΔP	=	1405 kPa				
A		15,5	9,5	10,0	1,05	0,93
B		15,7	9,6	8,6	0,90	0,94
C		15,0	9,2	8,4	0,91	0,94
D		15,3	9,4	9,8	1,04	0,93

FT-30 membrane :

$C_f = 1,38 \text{ mmol/l}$; mg/l , 1-butanol

	(1)	(2)	(3)	(4)	(5)	(6)
ΔP	=	5620 kPa				
A		55,6	34,1	3,8	0,11	0,92
B		56,8	34,8	3,5	0,10	0,93
C		55,0	33,7	3,7	0,11	0,92
D		54,8	33,6	3,4	0,10	0,93
ΔP	=	4567 kPa				
A		44,7	27,4	3,0	0,11	0,92
B		44,9	27,5	3,0	0,11	0,92
C		43,7	26,8	3,2	0,12	0,91
D		43,2	26,5	2,9	0,11	0,92
ΔP	=	3513 kPa				
A		33,9	20,8	2,3	0,11	0,92
B		33,4	20,5	2,5	0,12	0,91
C		32,7	20,1	2,4	0,12	0,91
D		32,8	20,1	2,2	0,11	0,92
ΔP	=	2459 kPa				
A		24,5	15,0	1,8	0,12	0,91
B		23,7	14,5	1,7	0,12	0,91
C		22,7	13,9	1,9	0,14	0,90
D		23,0	14,1	2,0	0,14	0,90

ΔP	=	1405 kPa				
A		13,4	8,2	1,4	0,17	0,88
B		13,5	8,2	1,2	0,15	0,89
C		12,7	7,8	1,2	0,15	0,89
D		12,9	7,9	1,4	0,18	0,87

SEPA-99 membrane (Permeate flux in $\text{m}\ell/45 \text{ min}$) :

$C_f = 1,38 \text{ mmol}/\ell$; $102 \text{ mg}/\ell$, 1-butanol

(1)	(2)	(3)	(4)	(5)	(6)	
ΔP	=	5620 kPa				
A		25,4	5,2	5,6	1,08	0,22
B		28,4	5,8	6,2	1,07	0,23
C		30,3	6,2	6,8	1,10	0,20
D		28,9	5,9	6,1	1,04	0,25
ΔP	=	4567 kPa				
A		20,1	4,1	4,8	1,16	0,16
B		20,6	4,2	4,7	1,13	0,18
C		21,5	4,4	5,1	1,15	0,16
D		22,5	4,6	5,1	1,10	0,20
ΔP	=	3513 kPa				
A		15,6	3,2	3,6	1,14	0,17
B		15,7	3,2	3,6	1,13	0,17
C		17,6	3,6	4,1	1,14	0,17
D		16,6	3,4	3,8	1,12	0,19
ΔP	=	2459 kPa				
A		11,7	2,4	2,8	1,16	0,16
B		12,2	2,5	2,9	1,14	0,17
C		12,7	2,6	2,9	1,13	0,18
D		11,7	2,4	2,6	1,10	0,20

$\Delta P = 1405 \text{ kPa}$

A	6,9	1,4	1,6	1,17	0,15
B	6,9	1,4	1,6	1,14	0,17
C	7,8	1,6	1,8	1,14	0,17
D	10,3	2,1	2,3	1,10	0,20

FT-30 membrane, 1-butanol :
 $\Delta P = 1405 \text{ kPa}$

$C_{f1} = 3,40 \text{ mmol}/\ell$

	(1)	(2)	(3)	(4)	(5)	(6)
A	13,7		8,4	4,0	0,48	0,86
B	13,5		8,3	3,1	0,37	0,89
C	13,2		8,1	3,0	0,37	0,89
D	13,7		8,4	2,9	0,34	0,90

$C_{f2} = 6,49 \text{ mmol}/\ell$

A	13,5		8,3	3,6	0,44	0,87
B	13,5		8,3	2,8	0,34	0,90
C	13,1		8,0	3,0	0,37	0,89
D	13,4		8,2	2,8	0,34	0,90

$C_{f3} = 12,47 \text{ mol}/\ell$

A	13,4		8,2	3,0	0,37	0,89
B	13,2		8,1	3,0	0,37	0,89
C	12,9		7,9	2,7	0,34	0,90
D	12,9		7,9	2,7	0,34	0,90

$C_{f4} = 20,42 \text{ mmol}/\ell$

A	13,2		8,1	2,8	0,34	0,90
B	13,2		8,1	3,0	0,37	0,89
C	12,9		7,9	2,9	0,37	0,89
D	12,7		7,8	2,7	0,34	0,90

TABLE B6

FT-30 membrane :

 $C_f = 3,95 \text{ mmol}/\ell$; $293 \text{ mg}/\ell$, 2-butanol

	(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa					
A	60,4		37,0	2,6	0,07	0,98
B	58,6		35,9	2,2	0,06	0,98
C	61,7		37,8	2,3	0,06	0,98
D	60,5		37,1	2,6	0,07	0,98
$\Delta P =$	2810 kPa					
A	29,7		18,2	2,2	0,12	0,97
B	29,0		17,8	2,3	0,13	0,97
C	30,0		18,4	2,4	0,13	0,97
D	29,4		18,0	2,3	0,13	0,97
$\Delta P =$	1405 kPa					
A	14,8		9,1	1,5	0,16	0,96
B	14,5		8,9	1,2	0,13	0,97
C	15,0		9,2	1,8	0,20	0,95
D	14,7		9,0	1,5	0,17	0,96

FT-30 membrane :

 $C_f = 11,9 \text{ mmol}/\ell$; $882 \text{ mg}/\ell$, 2-butanol

	(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa					
A	57,1		35,0	8,4	0,24	0,98
B	55,5		34,0	8,8	0,26	0,98
C	57,5		35,2	12,7	0,36	0,97
D	57,2		35,0	7,7	0,22	0,98

$\Delta P = 2810 \text{ kPa}$

A	27,9	17,1	5,8	0,34	0,97
B	26,1	16,0	5,4	0,34	0,97
C	28,0	17,1	7,9	0,46	0,96
D	26,8	16,4	4,9	0,30	0,97

$\Delta P = 1405 \text{ kPa}$

A	14,0	8,6	3,9	0,45	0,96
B	13,7	8,4	4,1	0,49	0,96
C	14,2	8,7	5,2	0,60	0,95
D	13,8	8,4	2,7	0,32	0,97

TABLE B7

FT-30 membrane :

 $C_f = 2,40 \text{ mmol/l}; 178 \text{ mg/l}$, 2-methyl-1-propanol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa				
A	63,3	38,8	1,9	0,05	0,98
B	62,0	38,0	1,5	0,04	0,98
C	60,2	36,9	0,7	0,02	0,99
D	63,1	38,7	1,5	0,04	0,98
$\Delta P =$	2810 kPa				
A	32,8	20,1	1,0	0,05	0,98
B	32,3	19,8	1,4	0,07	0,97
C	30,7	18,8	0,9	0,05	0,98
D	33,3	20,4	1,6	0,08	0,97
$\Delta P =$	1405 kPa				
A	17,0	10,4	0,8	0,08	0,97
B	15,8	9,7	1,0	0,10	0,96
C	15,7	9,6	0,9	0,09	0,97
D	17,3	10,6	0,7	0,07	0,97

TABLE B8

FT-30 membrane :

 $C_f = 2,83 \text{ mmol/l}; 210 \text{ mg/l}$, 2-methyl-2-propanol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P = 5620 \text{ kPa}$					
A	62,0	38,0	1,5	0,04	0,986
B	63,3	38,8	1,2	0,03	0,989
C	60,7	37,2	1,1	0,03	0,989
D	59,4	36,4	1,1	0,03	0,989
$\Delta P = 2810 \text{ kPa}$					
A	31,5	19,3	0,8	0,04	0,986
B	32,6	20,0	0,8	0,04	0,986
C	31,2	19,1	0,8	0,04	0,986
D	30,5	18,7	0,7	0,04	0,986
$\Delta P = 1405 \text{ kPa}$					
A	14,8	9,1	0,5	0,06	0,979
B	14,9	9,1	0,5	0,05	0,982
C	14,5	8,9	0,4	0,05	0,982
D	14,2	8,7	0,4	0,05	0,982

FT-30 membrane :

 $C_f = 32,12 \text{ mmol/l}; 2380 \text{ mg/l}$, 2-methyl-2-propanol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P = 5620 \text{ kPa}$					
A	55,7	34,1	5,5	0,16	0,995
B	60,4	37,0	7,4	0,20	0,994
C	57,5	35,4	7,8	0,22	0,993
D	55,2	33,8	6,8	0,20	0,994
$\Delta P = 2810 \text{ kPa}$					
A	25,8	15,8	4,1	0,26	0,992
B	27,4	16,8	5,2	0,31	0,990
C	26,4	16,2	5,2	0,32	0,990
D	25,9	15,9	4,8	0,30	0,990

$\Delta P = 1405 \text{ kPa}$

A	13,4	8,2	3,9	0,48	0,985
B	14,0	8,6	4,7	0,55	0,983
C	13,7	8,4	5,0	0,60	0,982
D	13,3	8,2	5,0	0,60	0,982

SEPA-99 membrane (Permeate flux in $\text{m}\ell/45 \text{ min}$) :

$C_f = 2,83 \text{ mmol}/\ell$; $210 \text{ mg}/\ell$, 2-methyl-2-propanol

	(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P = 5620 \text{ kPa}$						
A	29,4	6,0	2,2	0,37	0,87	
B	27,9	5,7	2,6	0,45	0,84	
C	28,9	5,9	3,0	0,50	0,82	
D	30,3	6,2	2,9	0,46	0,84	
$\Delta P = 2810 \text{ kPa}$						
A	14,2	2,9	1,6	0,56	0,80	
B	13,2	2,7	1,5	0,55	0,80	
C	13,2	2,7	1,4	0,52	0,79	
D	14,7	3,0	1,7	0,56	0,80	
$\Delta P = 1405 \text{ kPa}$						
A	6,9	1,4	0,8	0,56	0,80	
B	6,4	1,3	0,7	0,52	0,79	
C	5,9	1,2	0,8	0,70	0,75	
D	7,8	1,6	0,8	0,50	0,82	

TABLE B9

FT-30 membrane :

 $C_f = 4,28 \text{ mmol}/\ell; 377 \text{ mg}/\ell, 1\text{-pentanol}$

	(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P = 5620 \text{ kPa}$						
A	57,4		35,2	7,4	0,21	0,95
B	58,9		36,1	8,4	0,26	0,94
C	59,9		36,7	11,0	0,30	0,93
D	58,7		36,0	9,4	0,26	0,94
$\Delta P = 2810 \text{ kPa}$						
A	27,9		17,1	5,8	0,34	0,92
B	29,0		17,8	6,2	0,35	0,92
C	29,4		18,0	6,8	0,38	0,91
D	27,1		16,6	5,0	0,30	0,93
$\Delta P = 1405 \text{ kPa}$						
A	13,7		8,4	3,9	0,47	0,89
B	13,9		8,5	3,7	0,43	0,90
C	14,0		8,6	4,4	0,51	0,88
D	13,4		8,2	3,6	0,44	0,90

FT-30 membrane :

 $\Delta P = 1405 \text{ kPa}, 1\text{-pentanol}$ $C_{f0} = \text{Pure water}$

	(1)	(2)	(3)	(4)	(5)	(6)
A	16,1		9,9			
B	16,5		10,1			
C	16,1		9,9			
D	12,2		7,5			
$C_{f1} = 0,67 \text{ mmol}/\ell, 59 \text{ mg}/\ell$						
A	15,3		9,4	0,7	0,08	0,88
B	16,0		9,8	0,8	0,08	0,88
C	15,3		9,4	0,7	0,07	0,89
D	12,1		7,4	0,4	0,06	0,91

$C_{f2} = 2,36 \text{ mol}/\ell, 208 \text{ mg}/\ell$

A	15,0	9,2	3,0	0,33	0,86
B	15,5	9,5	2,5	0,26	0,89
C	15,0	9,2	2,2	0,24	0,90
D	11,6	7,1	1,6	0,23	0,90

$C_{f3} = 5,91 \text{ mmol}/\ell, 521 \text{ mg}/\ell$

A	14,2	8,7	6,2	0,71	0,88
B	14,8	9,1	6,4	0,70	0,88
C	14,2	8,7	5,1	0,59	0,90
D	10,8	6,6	3,5	0,53	0,91

$C_{f4} = 13,75 \text{ mmol}/\ell, 1212 \text{ mg}/\ell$

A	14,0	8,6	14,2	1,65	0,88
B	14,2	8,7	11,9	1,37	0,90
C	13,7	8,4	11,6	1,38	0,90
D	-	-	-	-	-

TABLE B10

FT-30 membrane :

 $C_f = 0,88 \text{ mmol/l}$; 90 mg/l , 1-hexanol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P = 5620 \text{ kPa}$					
A	54,6	33,5	1,3	0,04	0,95
B	52,2	32,0	1,3	0,04	0,95
C	51,1	31,3	1,3	0,04	0,96
D	52,0	31,9	1,3	0,04	0,96
$\Delta P = 3513 \text{ kPa}$					
A	36,5	22,4	1,1	0,05	0,94
B	33,3	20,4	0,8	0,04	0,95
C	32,6	20,0	1,0	0,05	0,94
D	33,1	20,3	1,0	0,05	0,94
$\Delta P = 2810 \text{ kPa}$					
A	29,0	17,8	1,1	0,06	0,93
B	26,6	16,3	0,8	0,05	0,94
C	25,9	15,9	0,8	0,05	0,94
D	26,6	16,3	0,8	0,05	0,94
$\Delta P = 2108 \text{ kPa}$					
A	22,2	13,6	1,0	0,07	0,92
B	20,1	12,3	0,7	0,06	0,93
C	19,7	12,1	0,6	0,05	0,94
D	20,2	12,4	0,6	0,05	0,94
$\Delta P = 1405 \text{ kPa}$					
A	14,7	9,0	0,6	0,07	0,92
B	12,9	7,9	0,5	0,06	0,93
C	12,6	7,7	0,5	0,06	0,93
D	13,1	8,0	0,6	0,07	0,92

SEPA-99 membrane (Permeate flux in ml/45 min) :

$C_f = 0,88 \text{ mmol/l}$; 90 mg/l , 1-hexanol

	(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa					
A	24,0		4,9	4,0	0,82	0,07
B	25,4		5,2	4,1	0,79	0,10
C	27,4		5,6	4,7	0,84	0,05
D	24,5		5,0	4,0	0,80	0,09
$\Delta P =$	3513 kPa					
A	15,2		3,1	2,5	0,81	0,08
B	16,1		3,3	2,7	0,81	0,08
C	16,6		3,4	2,7	0,79	0,10
D	15,2		3,1	2,4	0,78	0,11
$\Delta P =$	2810 kPa					
A	12,2		2,5	2,0	0,80	0,09
B	12,7		2,6	2,1	0,80	0,09
C	13,7		2,8	2,2	0,79	0,10
D	13,2		2,7	2,2	0,80	0,09
$\Delta P =$	2108 kPa					
A	9,8		2,0	1,6	0,81	0,08
B	10,8		2,2	1,7	0,79	0,10
C	11,7		2,4	1,8	0,77	0,12
D	11,7		2,4	1,9	0,81	0,08
$\Delta P =$	1405 kPa					
A	6,4		1,3	1,0	0,78	0,11
B	7,3		1,5	1,2	0,82	0,07
C	7,3		1,5	1,2	0,77	0,12
D	7,8		1,6	1,2	0,78	0,11

TABLE III

FT-30 membrane :

 $C_f = 0,516 \text{ mmol/l}$; 60 mg/l , 1-heptanol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa				
A	58,0	35,6	0,7	0,02	0,96
B	55,8	34,2	0,7	0,02	0,96
C	58,7	36,0	0,7	0,02	0,96
D	55,5	34,0	0,7	0,02	0,97
$\Delta P =$	2810 kPa				
A	29,2	17,9	0,5	0,03	0,95
B	28,2	17,3	0,5	0,03	0,95
C	30,3	18,6	0,5	0,03	0,95
D	28,1	17,2	0,5	0,03	0,95
$\Delta P =$	1405 kPa				
A	13,9	8,5	0,4	0,05	0,90
B	13,5	8,3	0,6	0,07	0,87
C	14,4	8,8	0,4	0,05	0,90
D	13,7	8,4	0,4	0,05	0,91

FT-30 membrane :

 $C_f = 4,29 \text{ mmol/l}$; 498 mg/l , 1-heptanol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa				
A	44,0	27,1	4,6	0,17	0,96
B	43,9	26,9	4,6	0,17	0,96
C	44,7	27,4	5,7	0,21	0,95
D	43,1	26,4	3,4	0,13	0,97
$\Delta P =$	2810 kPa				
A	22,2	13,6	2,9	0,21	0,95
B	22,0	13,5	2,7	0,20	0,95
C	23,0	14,1	3,1	0,22	0,95
D	21,9	13,4	2,4	0,18	0,96

$\Delta P = 1405 \text{ kPa}$

A	11,3	6,9	2,7	0,39	0,91
B	11,3	6,9	2,3	0,34	0,92
C	11,7	7,2	2,7	0,37	0,91
D	10,9	6,7	2,3	0,34	0,92

FT-30 membrane :

$C_f = 9,90 \text{ mmol/l}$; 1150 mg/l , 1-heptanol

(1) (2) (3) (4) (5) (6)

$\Delta P = 5620 \text{ kPa}$

A	34,9	21,4	10,9	0,51	0,95
B	34,6	21,2	8,5	0,40	0,96
C	35,7	22,9	8,5	0,39	0,96
D	33,9	20,8	6,2	0,30	0,97

$\Delta P = 2810 \text{ kPa}$

A	18,6	11,4	6,7	0,59	0,94
B	17,9	11,0	5,7	0,52	0,95
C	19,4	11,9	4,8	0,40	0,96
D	17,8	10,0	4,3	0,39	0,96

$\Delta P = 1405 \text{ kPa}$

A	9,1	5,6	4,4	0,79	0,92
B	9,3	5,7	3,9	0,69	0,93
C	9,8	6,0	4,8	0,80	0,92
D	8,8	5,4	3,8	0,70	0,93

TABLE B12

FT-30 membrane :

 $C_f = 1,382 \text{ mmol/l}$; 130 mg/l, phenol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa				
A	60,7	37,2	3,2	0,085	0,94
B	64,4	39,5	3,8	0,096	0,93
C	66,4	40,7	3,9	0,096	0,93
D	63,8	39,1	4,1	0,106	0,92
$\Delta P =$	4216 kPa				
A	45,8	28,1	2,7	0,096	0,93
B	46,5	28,5	2,7	0,096	0,93
C	47,8	29,3	3,1	0,106	0,92
D	46,0	28,2	3,0	0,106	0,92
$\Delta P =$	2810 kPa				
A	30,3	18,6	2,0	0,106	0,92
B	31,0	19,0	1,8	0,096	0,93
C	32,5	19,9	2,1	0,106	0,92
D	30,2	18,5	2,4	0,128	0,91
$\Delta P =$	1405 kPa				
A	15,0	9,2	1,7	0,181	0,87
B	15,5	9,5	1,7	0,181	0,87
C	16,1	9,9	1,7	0,170	0,88
D	15,0	9,2	1,7	0,181	0,87

FT-30 membrane :

 $C_f = 2,55 \text{ mmol/l}$; 240 mg/l, phenol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa				
A	56,4	34,6	5,2	0,149	0,94
B	53,0	32,5	4,8	0,149	0,94
C	51,9	31,8	5,8	0,181	0,93
D	52,2	32,0	4,8	0,149	0,94

ΔP	=	4216 kPa				
A		43,7	26,8	4,9	0,181	0,93
B		41,8	25,6	4,6	0,181	0,93
C		40,8	25,0	5,1	0,202	0,92
D		41,3	25,3	5,1	0,202	0,92
ΔP	=	2810 kPa				
A		29,7	18,2	3,7	0,202	0,92
B		28,7	17,6	3,6	0,202	0,92
C		28,2	17,3	4,0	0,234	0,91
D		28,5	17,5	3,5	0,202	0,92
ΔP	=	1405 kPa				
A		15,0	9,2	3,0	0,329	0,87
B		14,5	8,9	2,9	0,329	0,87
C		14,4	8,8	2,9	0,329	0,87
D		14,5	8,9	2,7	0,308	0,88
ΔP	=	562 kPa				
A		6,0	3,7	2,6	0,691	0,73
B		5,7	3,5	2,3	0,659	0,74
C		5,5	3,4	2,4	0,712	0,72
D		5,5	3,4	2,3	0,691	0,73

SEPA-99 membrane (Permeate Flux in ml/45 min) :

$C_f = 2,55 \text{ mmol/l}; 240 \text{ mg/l},$

	(1)	(2)	(3)	(4)	(5)	(6)
ΔP	=	5620 kPa				
A		28,4	5,8	15,4	2,66	-0,05
B		33,2	5,8	19,9	2,92	-0,15
C		28,9	5,9	15,0	2,55	0,0
D		30,3	6,2	16,1	2,60	-0,02

ΔP	=	2810 kPa				
A		15,2	3,1	7,9	2,55	0,0
B		17,6	3,6	10,2	2,82	-0,10
C		16,1	3,3	8,8	2,66	-0,05
D		16,6	3,4	8,7	2,55	0,0
ΔP	=	1405 kPa				
A		7,3	1,5	3,8	2,50	0,02
B		8,8	1,8	4,6	2,55	0,0
C		7,8	1,6	3,9	2,45	0,04
D		8,3	1,7	3,8	2,24	0,12

FT-30 membrane :

$C_f = 21,25 \text{ mmol/l}; 2000 \text{ mg/l, phenol}$

(1)	(2)	(3)	(4)	(5)	(6)	
ΔP	=	5620 kPa				
A		44,7	27,4	35,1	1,28	0,94
B		43,7	26,8	34,3	1,26	0,94
C		42,7	26,2	33,5	1,27	0,94
D		44,0	27,0	34,6	1,27	0,94
ΔP	=	2810 kPa				
A		20,6	12,6	18,8	1,49	0,93
B		20,1	12,3	20,9	1,70	0,92
C		19,7	12,1	20,6	1,67	0,92
D		20,1	12,3	20,7	1,68	0,92
ΔP	=	1405 kPa				
A		9,3	5,7	13,3	2,34	0,89
B		8,8	5,4	13,8	2,55	0,88
C		8,6	5,3	13,5	2,58	0,88
D		8,8	5,4	14,9	2,76	0,87

FT-30 membrane :

$C_f = 42,51 \text{ mmol/l}$; 4000 mg/l , phenol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa				
A	39,2	24,0	51,1	2,13	0,95
B	36,7	22,5	57,4	2,55	0,94
C	36,4	22,3	56,7	2,51	0,94
D	36,9	22,6	57,4	2,53	0,94
$\Delta P =$	2810 kPa				
A	17,8	10,9	32,5	2,98	0,93
B	17,1	10,5	35,8	3,42	0,92
C	16,8	10,3	35,0	3,40	0,92
D	17,0	10,4	35,8	3,44	0,92
$\Delta P =$	1405 kPa				
A	7,7	4,7	26,0	5,53	0,87
B	7,4	4,4	23,0	5,10	0,88
C	7,0	4,3	23,8	5,53	0,87
D	7,2	4,4	24,3	5,54	0,87

FT-30 membrane (Jv in $\text{ml}/30 \text{ min}$) :

$C_f = 69,07 \text{ mmol/l}$; 6500 mg/l , phenol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa				
A	63,3	19,4	80,3	4,14	0,94
B	60,0	18,4	76,4	4,15	0,94
C	59,0	18,1	86,0	4,75	0,93
D	59,4	18,2	84,3	4,63	0,92
$\Delta P =$	2810 kPa				
A	29,4	9,0	50,0	5,52	0,92
B	28,1	8,6	47,2	5,49	0,92
C	27,4	8,4	51,9	6,18	0,91
D	27,7	8,5	46,6	5,48	0,92

$\rightarrow P = 1405 \text{ kPa}$

A	13,1	4,0	36,0	9,0	0,87
B	12,1	3,7	32,2	8,8	0,87
C	11,7	3,6	33,8	9,4	0,86
D	11,7	3,6	33,5	9,3	0,86

TABLE B13

FT-30 membrane :

 $C_f = 15,2 \text{ mmol/l}; 1640 \text{ mg/l}, 4\text{-methyl phenol}$

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P = 2108 \text{ kPa}$					
A	13,1	8,0	7,3	0,91	0,94
B	12,6	7,7	7,5	0,97	0,93
C	13,7	8,4	8,2	0,98	0,93
D	14,0	8,6	9,8	1,14	0,92
$\Delta P = 3513 \text{ kPa}$					
A	23,0	14,1	8,6	0,61	0,96
B	21,7	13,3	9,2	0,69	0,95
C	23,3	14,3	10,0	0,70	0,95
D	24,3	14,9	11,0	0,74	0,95
$\Delta P = 5620 \text{ kPa}$					
A	34,3	21,0	9,7	0,46	0,97
B	32,8	20,1	11,9	0,59	0,96
C	34,3	21,0	12,8	0,61	0,96
D	37,0	22,7	8,8	0,39	0,97
$\Delta P = 2810 \text{ kPa}$					
A	17,6	10,8	9,7	0,90	0,94
B	17,1	10,5	10,1	0,96	0,93
C	17,3	10,6	9,6	0,91	0,94
D	17,1	11,5	10,0	0,87	0,94
$\Delta P = 1405 \text{ kPa}$					
A	8,3	5,1	6,9	1,35	0,91
B	8,2	5,0	6,6	1,31	0,91
C	7,8	4,8	7,1	1,48	0,90
D	8,6	5,3	7,3	1,38	0,91

FT-30 membrane, 4-methyl phenol :

$\Delta P = 1405 \text{ kPa}$

(1)	(2)	(3)	(4)	(5)	(6)
$C_{f1} = 0,407 \text{ mmol/l, } 44 \text{ mg/l}$					
A	15,5	9,5	0,35	0,037	0,91
B	14,4	8,8	0,39	0,044	0,96
C	14,4	8,8	0,33	0,038	0,90
D	15,5	9,5	0,35	0,037	0,91
$C_{f2} = 1,42 \text{ mmol/l, } 150 \text{ mg/l}$					
A	13,5	8,3	1,0	0,120	0,92
B	13,1	8,0	1,1	0,133	0,91
C	12,7	7,8	0,9	0,126	0,91
D	13,7	8,4	1,1	0,127	0,91
$C_{f3} = 3,48 \text{ mmol/l, } 376 \text{ mg/l}$					
A	12,9	7,9	2,7	0,343	0,90
B	11,9	7,3	2,4	0,328	0,91
C	11,7	7,2	2,3	0,325	0,91
D	12,9	7,9	3,0	0,380	0,89
$C_{f4} = 8,97 \text{ mmol/l, } 970 \text{ mg/l}$					
A	10,3	6,3	5,1	0,815	0,91
B	9,6	5,9	5,2	0,889	0,90
C	9,5	5,8	4,8	0,828	0,91
D	10,1	6,2	5,2	0,840	0,91
$C_{f5} = 13,9 \text{ mmol/l, } 1503 \text{ mg/l}$					
A	8,8	5,4	5,8	1,08	0,92
B	8,3	5,1	6,3	1,23	0,91
C	8,3	5,1	6,1	1,20	0,91
D	9,1	5,6	7,1	1,26	0,91

TABLE B14

FT-30 membrane :

 $C_f = 1,88 \text{ mmol/l}$; 230 mg/l , 4-ethyl phenol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa				
A	54,0	33,1	2,2	0,067	0,97
B	48,3	29,6	2,1	0,070	0,96
C	52,2	32,0	2,2	0,070	0,96
D	50,2	30,8	2,2	1,071	0,97
$\Delta P =$	3513 kPa				
A	33,9	20,8	1,5	0,070	0,96
B	31,5	19,3	1,4	0,072	0,96
C	32,6	20,0	1,8	0,088	0,95
D	31,2	19,1	1,5	0,079	0,96
$\Delta P =$	2459 kPa				
A	24,0	14,7	1,1	0,073	0,96
B	22,0	13,5	1,2	0,086	0,95
C	23,0	14,1	1,3	0,091	0,95
D	21,9	13,4	1,2	0,092	0,95
$\Delta P =$	1405 kPa				
A	13,5	8,3	1,0	0,117	0,94
B	11,9	7,3	1,0	0,135	0,93
C	12,4	7,6	1,0	0,132	0,93
D	12,1	7,4	0,9	0,125	0,93

TABLE B15

FT-30 membrane :

$C_f = 1,514 \text{ mmol/l}$, 185 mg/l , 2,6 dimethyl phenol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P = 5620 \text{ kPa}$					
A	52,4	32,1	0,4	0,014	0,991
B	50,2	30,8	0,3	0,009	0,994
C	46,8	28,7	0,4	0,013	0,991
D	47,6	29,2	0,6	1,021	0,986
$\Delta P = 2810 \text{ kPa}$					
A	25,9	15,9	0,5	0,033	0,978
B	24,3	14,9	0,4	0,030	0,980
C	23,2	14,2	0,4	0,030	0,980
D	25,1	15,4	0,4	0,024	0,984
$\Delta P = 1405 \text{ kPa}$					
A	12,2	7,5	0,3	0,038	0,975
B	12,1	7,4	0,2	0,033	0,978
C	11,7	7,2	0,3	0,048	0,968
D	12,2	7,5	0,2	0,032	0,979

SEPA-99 membrane (Permeate flux in $\text{m}\ell/45 \text{ min}$) :

$C_f = 1,514 \text{ mmol/l}$; 185 mg/l , 2,6 dimethyl phenol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P = 5620 \text{ kPa}$					
A	26,4	5,4	0,7	1,22	0,19
B	25,4	5,2	0,6	1,21	0,20
C	27,9	5,7	0,8	1,35	0,11
D	24,0	4,9	0,6	1,15	0,24

$\Delta P = 2810 \text{ kPa}$

A	12,7	2,6	2,8	1,09	0,28
B	12,2	2,5	3,0	1,22	0,20
C	13,7	2,8	3,4	1,20	0,20
D	11,3	2,3	2,6	1,12	0,26

 $\Delta P = 1405 \text{ kPa}$

A	5,9	1,2	1,0	0,85	0,44
B	5,9	1,2	0,9	0,75	0,50
C	6,4	1,3	1,2	0,91	0,40
D	4,9	1,0	0,8	0,84	0,44

TABLE B16

FT-30 membrane :

 $C_f = 0,43 \text{ mmol}/\ell$; $59 \text{ mg}/\ell$, 4-n-propyl phenol

(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P = 5620 \text{ kPa}$					
A	52,2	32,0	0,3	0,008	0,981
B	53,3	32,7	0,2	0,006	0,986
C	51,2	31,4	0,3	0,009	0,979
D	47,6	29,2	0,2	0,008	0,982
$\Delta P = 4567 \text{ kPa}$					
A	43,7	26,8	0,2	0,009	0,978
B	44,0	27,0	0,2	0,006	0,985
C	43,1	26,4	0,2	0,010	0,976
D	41,8	25,6	0,2	0,009	0,978
$\Delta P = 3513 \text{ kPa}$					
A	34,4	21,1	0,2	0,009	0,978
B	34,6	21,2	0,1	0,006	0,985
C	33,1	20,3	0,2	0,010	0,976
D	32,6	20,0	0,2	0,009	0,978
$\Delta P = 2459 \text{ kPa}$					
A	23,5	14,4	0,1	0,010	0,976
B	24,3	14,9	0,1	0,008	0,981
C	21,9	13,4	0,1	0,011	0,974
D	21,7	13,3	0,1	0,011	0,974
$\Delta P = 1405 \text{ kPa}$					
A	12,7	7,8	0,1	0,017	0,961
B	13,4	8,2	0,1	0,013	0,970
C	12,4	7,6	0,1	0,017	0,961
D	12,4	7,6	0,1	0,015	0,964

SEPA-99 membrane (Permeate flux in ml/45 min) :

$C_f = 0,43 \text{ mmol/l}$; 59 mg/l , 4-n-propyl phenol

	(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P =$	5620 kPa					
A	28,4		5,8	2,3	0,40	0,08
B	26,9		5,5	2,3	0,43	0,0
C	27,4		5,6	2,4	0,42	0,01
D	26,4		5,4	2,3	0,42	0,02
$\Delta P =$	4567 kPa					
A	23,0		4,7	1,8	0,38	0,10
B	22,0		4,5	1,8	0,40	0,06
C	23,0		4,7	1,9	0,41	0,04
D	22,0		4,5	1,9	0,43	0,00
$\Delta P =$	3513 kPa					
A	18,6		3,8	1,5	0,39	0,08
B	17,6		3,6	1,4	0,40	0,06
C	17,6		3,6	1,5	0,42	0,02
D	17,1		3,5	1,5	0,42	0,02
$\Delta P =$	2459 kPa					
A	14,2		2,9	1,0	0,35	0,19
B	13,2		2,7	1,0	0,36	0,15
C	13,2		2,7	1,0	0,38	0,12
D	12,7		2,6	1,0	0,37	0,15
$\Delta P =$	1405 kPa					
A	8,3		1,7	0,5	0,28	0,34
B	7,8		1,6	0,5	0,30	0,29
C	7,8		1,6	0,5	0,30	0,30
D	7,8		1,6	0,5	0,32	0,25

TABLE B17

FT-30 membrane :

$C_f = 1,17 \text{ mmol/l}$; 159 mg/l , 4 isopropyl phenol

	(1)	(2)	(3)	(4)	(5)	(6)
$\Delta P = 5620 \text{ kPa}$						
A	49,9		30,6	0,4	0,014	0,988
B	48,0		29,4	0,4	0,014	0,988
C	50,7		31,1	0,4	0,015	0,987
D	42,9		26,3	0,4	0,104	0,988
$\Delta P = 4216 \text{ kPa}$						
A	38,7		23,7	0,4	0,015	0,987
B	37,7		23,1	0,4	0,015	0,987
C	39,6		24,3	0,4	0,016	0,986
D	33,0		20,2	0,4	0,015	0,987
$\Delta P = 2810 \text{ kPa}$						
A	25,8		15,8	0,3	0,020	0,983
B	25,6		15,7	0,3	0,019	0,984
C	26,4		16,2	0,3	0,020	0,983
D	22,0		13,5	0,3	0,019	0,984
$\Delta P = 1405 \text{ kPa}$						
A	12,6		7,7	0,2	0,027	0,977
B	12,6		7,7	0,2	0,026	0,978
C	12,9		7,9	0,2	0,030	0,974
D	10,1		6,2	0,2	0,026	0,978

SEPA-99 membrane (Permeate flux in $\text{ml}/45 \text{ min}$) :

$C_f = 1,17 \text{ mmol/l}$; 159 mg/l , 4 isopropyl phenol

(1)	(2)	(3)	(4)	(5)	(6)
-----	-----	-----	-----	-----	-----

$\Delta P = 5620 \text{ kPa}$

A	18,6	3,8	3,5	0,91	0,22
B	17,1	3,5	3,4	0,87	0,26
C	18,6	3,8	3,5	0,90	0,23
D	18,6	3,8	3,6	0,94	0,20

$\Delta P = 4216 \text{ kPa}$

A	14,7	3,0	2,6	0,87	0,26
B	14,2	2,9	2,6	0,87	0,26
C	13,7	2,8	2,5	0,80	0,32
D	14,2	2,9	2,6	0,91	0,22

$P = 2810 \text{ kPa}$

A	9,8	2,0	1,6	0,76	0,30
B	9,3	1,9	1,8	0,78	0,19
C	9,3	1,9	1,7	0,87	0,26
D	9,3	1,9	1,4	0,71	0,36

$P = 1405 \text{ kPa}$

A	4,9	1,0	0,8	0,76	0,35
B	4,9	1,0	0,8	0,78	0,33
C	4,9	0,9	0,8	0,87	0,26
D	4,4	0,9	0,6	0,71	0,39

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WATER RECYCLING - FUTURE RESOURCE FOR CAPE TOWN

C F Schutte
Senior Adviser
Water Research Commission
P O Box 824
Pretoria, South Africa

H C J Beekman
Chief Engineer
Cape Town Municipality
Cape Town, South Africa

ABSTRACT

The fresh water resources available to Cape Town are limited. Projections for water supply and demand indicate that the fresh water sources will all be fully committed towards the middle of the 1990's. Unconventional sources, in particular water recycling will then be relied upon to meet demands.

The current status of a project aimed at the full scale recycling of reclaimed water and future planning for the project are described.

INTRODUCTION

South Africa is a relatively dry country rapidly approaching the point of maximum utilisation of conventional water resources for the country as a whole. Projections indicate that this point could be reached soon after the turn of the century. Certain areas, however, are using their supplies to the maximum and some supplies have already had to be augmented by measures such as the interbasin transfer of water. In order to make sufficient water available in future to sustain economic and industrial growth unconventional water resources such as desalination of brackish or seawater and the recycling of reclaimed water will have to be harnessed. Water reclamation and recycling has been identified as measures which could significantly contribute to solving the water problem by relieving some of the pressure on fresh water supplies.

Research and development on water reclamation have been in progress for almost two decades in South Africa and direct recycling of reclaimed water in the municipal supply has been practised since 1969 at Windhoek to supplement the water supply. Two other areas where water recycling will have to be implemented in the near future are the Pretoria-Witwatersrand-Vereeniging Complex and the Greater Cape Town area. This paper describes the water supply-demand situation in the Cape Town area, the role which water reclamation will have to play to augment conventional supplies and the progress with and planning for the implementation of full scale water reclamation in Cape Town.

WATER SUPPLY AND DEMAND

Cape Town was founded in 1652 when the first Dutch settlers landed at the southern tip of Africa. Today the population of the Cape Town Metropolitan area is about 1,5 million with a population growth rate of about 3% per annum.

The area has a mediterranean climate with rainfall mainly in winter and a long mainly dry summer season. The result of this rainfall pattern is an increased demand for water during the dry summer months especially for irrigation and gardening purposes and a much-reduced demand during winter. The precipitation varies considerably between mountain and flat areas, and between coastal and inland areas.(1)

The area is not heavily industrialised although a large number of smaller secondary manufacturing industries (such as textiles) as well as a small number of heavy industries do exist.

The early water supply to Cape Town was derived from springs and creeks on Table Mountain. These sources were impounded later through construction of a number of smaller dams. Due to continued developments it became necessary to transport water from more distant sources from catchments to the east of Cape Town and as a result water could be supplied to local authorities en route. At present 13 local authorities and peri-urban areas receive water in bulk from Cape Town amounting to about 50% of the total volume supplies. See figure 1 for orientation.

The assured yield of currently available sources indicated in Table 1 amounts to $166 \times 10^6 \text{ m}^3/\text{a}$. The current water demand is about $195 \times 10^6 \text{ m}^3/\text{a}$ and is being met by temporary allocations from other sources.

The water demand of the area increased at an average rate of 6,12% per annum during the past 20 year period. This growth rate was used to project the water demand for the area for the period up to 2005 as indicated in Table II.(2)

Future projects which could be developed to meet projected demands up to 1995 include Theewaterskloof (1982), Cape Flats Aquifer and other smaller sources (1986), Palmiet River (1989). See figure 2.

LONG TERM PLANNING FOR THE RECLAMATION AND RECYCLING OF WATER IN GREATER CAPE TOWN

The conventional fresh water resources available to Cape Town will only be able to meet projected demands up to 1995. Beyond this date unconventional resources such as water recycling will have to be harnessed to meet demands.

Long term planning for the reclamation and recycling of water commenced during the latter half of the 1960's when a detailed survey was carried out of the quantities and qualities of sewage flows in the area and projections were made of future flows. The main objective of these studies was to develop a master plan for

- (i) the modernization of the sewerage systems and sewage purification facilities in the area,
- (ii) the strategic location of sewage purification works on a regional basis,
- (iii) the diversion of sewage effluents from industrial areas to a centralised purification works,
- (iv) the purification of sewage effluents from essentially domestic origin at regional works and the reclamation of these effluents for reuse in future.

This master plan was accepted by the Cape Town City Council, and an advanced stage of implementation has been reached.

It was subsequently decided to establish a 4500 m³/d prototype demonstration water reclamation plant at the new Cape Flats sewage works, an activated sludge plant designed for biological nitrogen and phosphorus removal. The reclamation plant is currently under construction and will be used for developing design and operating criteria for full scale water reclamation and will also serve as a demonstration facility.

Concurrently with these developments another aspect was investigated viz the geohydrology of the coastal sand deposits of the Cape Flats area and its suitability to serve as a reservoir for the storage of reclaimed water. It was concluded from these studies that the deposits which extend to depths up to 50 m below sea level can serve as a storage reservoir. (3) However, the studies were discontinued since the aquifer is now being developed for abstraction of ground water. Once the full yield of the aquifer is realised further consideration will be given to the possible infiltration and storage of reclaimed water in the aquifer.

PRESENT STATUS OF THE WATER RECLAMATION PROJECT

The approach being followed for the eventual full scale implementation of water recycling is firstly, to establish a 4500 m³/d prototype demonstration water reclamation plant capable of producing water of potable quality. This will be followed by investigations concerning all aspects related to recycling of water for municipal and possibly irrigation use.

The plant is currently under construction and it is expected to be completed early in 1982. The plant comprises the treatment processes required to produce reclaimed water of potable quality, i.e. chemical clarification, filtration, breakpoint chlorination, active carbon adsorption and final chlorination. Pilot scale studies to investigate the effect of ozonation and chlorination on the performance of activated carbon and on reclaimed water quality are in progress. The findings of these investigations will determine if, and where ozonation will be included in the process configuration.

Provision is also made for investigating the application of small scale reverse osmosis units to treat a side stream of final reclaimed water as well as other process streams in order to assess the potential role of reverse osmosis as substitute to some of the "conventional" reclamation processes. A separate project on the pretreatment of secondary sewage effluents for reclamation by reverse osmosis is being conducted in parallel with the aforementioned investigations.

RESEARCH AND DEMONSTRATION PROGRAM

Optimisation

A program of commissioning and optimization of the various unit processes will start after completion of construction of the plant. It is expected that these optimization studies and related research will be completed towards the end of 1984. During this period performance will be monitored as fully as possible with special emphasis on analysis and removal of residual organic material in reclaimed water and mutagenic/carcinogenic testing of concentrates of feed and final water as well as certain process streams.

Experience gained at the Windhoek water reclamation plant and the Stander reclamation plant in Pretoria indicate that the plant should be experienced with optimization. However, it is realised that the characteristics of the secondary effluent to be reclaimed are somewhat different to those at the other locations mentioned and a sufficient period is therefore allowed to eliminate any possible problems which could arise.

The following will form the basis of the optimization program : maximum removal of turbidity, phosphorus and nitrogenous compounds, chemical oxygen demand, total organic chlorine, total organic halogens, volatile halogenated hydrocarbons, specific toxic compounds, micro-organisms and viruses, identification (and removal if necessary) of currently unknown compounds present at undesirable concentrations in the inflow.

Research and Development

During the optimisation stage some peripheral research will also be conducted. One aspect of importance is the possible application of reverse osmosis to replace some of the "conventional" reclamation processes with the added benefit of producing a desalinated product water. An earlier investigation aimed specifically at the application of reverse osmosis for water reclamation indicated that an excellent product could be produced but problems were experienced with reduced fluxes due to membrane fouling.

Evaluation of plant performance under production conditions

Once the plant has been fully optimised a continuous run will follow for a period of about one year, to test the performance and reliability of the plant under practical production conditions. This opportunity will also be used for demonstration purposes as part of a local and national public information programme to inform the public of the water supply-demand situation and the potential of water recycling to augment supplies.

Reuse

The stage will then be set for a final decision on the application of the reclaimed water from the prototype demonstration plant. The feasibility to recycle the 4500 m³/d of potable reclaimed water at a very high dilution ratio in the municipal supply for direct reuse will be considered.

Advantages of an extended demonstration run will be that a facility operating under real conditions will be available for training of operators for a future large scale plant.

Figure 3 gives a time schedule for the different aspects of the program aimed at the full scale implementation of water reclamation and recycling.

PUBLIC HEALTH ASPECTS RELATED TO THE RECYCLING OF WATER IN THE MUNICIPAL SUPPLY

High priority is being given to the development of criteria for drinking water derived from polluted sources all over the world. This view was also expressed at the Airlee workshop : Protocol development : Criteria and standards for potable reuse and feasible alternatives. In South Africa the Department of Health, Welfare and Pensions is in the process of developing a set of requirements and criteria for the recycling of

water in the municipal supply and these criteria are well known in 1982. These criteria are being formulated on the basis of data gained at the Windhoek and Stander water reclamation plants over a period of about a decade of operation, surveillance and research.

In addition to all the safety measures incorporated in a reclamation project for unrestricted reuse it is also considered essential that epidemiological studies be conducted on a population receiving reclaimed water in order to be able to identify any possible change in health patterns. Therefore, in view of the fact that reclaimed water might be introduced in the Cape Town municipal supply in the future it was decided to start with an epidemiological survey well before the possible introduction of reclaimed water so as to establish the background health patterns for future reference. A separate paper on this project will be presented later at this conference.

CONSIDERATION OF THE VARIOUS REUSE OPTIONS FOR CAPE TOWN

Generally speaking there are four possibilities for recycling reclaimed water. These are

Direct Recycling of Reclaimed Water in the Municipal Supply for Unrestricted Reuse

Direct recycling of reclaimed water for unrestricted use comprises the reclamation of water from secondary treated effluents to full potable quality and direct introduction into the municipal supply in admixture with other water. Direct recycling will be a feasible proposition for the reuse of relatively large volumes of reclaimed water. Demand for municipal supplies are ever increasing and additional supplies must continuously be found. Reclaimed water is a source that will always be available to satisfy part of increases in demand.

From a reticulation point of view there are a number of advantages in recycling of reclaimed water in the municipal supply viz pumping costs are kept to a minimum, evaporation losses of reclaimed water are minimized, no separate reticulation system is required. On the other hand greater care must be taken with the reclamation process and more safety barriers and greater reliability must be provided in comparison to conventional water treatment.

From an economic and practical engineering point of view direct recycling seems to be the most feasible reuse option for Cape Town and research has therefore been directed mainly at this route for recycling.

Simulated Indirect Reuse

The term "simulated indirect reuse" is used for the planned return of reclaimed water to a water body which is being used as a water supply source. All the water supply sources for the Cape Town area are surface dams and impoundments and the larger of these serve as sources for both municipal and irrigation waters. In returning reclaimed water to such a source it might be possible to get a bigger allocation for municipal use from the source. As far as Cape Town is concerned the distances to water supply dams and the altitudes at which they are located will not favour this mode of reuse, purely on economic considerations.

Another possibility for simulated indirect reuse is the reclamation of reclaimed water to the Cape Flats aquifer (4). This aquifer with an estimated yield of about $18 \times 10^6 \text{ m}^3/\text{a}$ will be developed for implementation towards 1986 (5). Once the yield of this source is fully utilised further consideration might be given to supplementing the ground water by infiltration of reclaimed water if found to be economically feasible.

Industrial Reuse

A survey was carried out during 1978 to assess the potential market for an industrial grade reclaimed water in the Greater Cape Town area (6). The total potential market was found to be about $7 \times 10^6 \text{ m}^3/\text{a}$ which is less than 5% of the total water usage in the area. In addition, the points of reuse are scattered over a large area making the distribution of reclaimed water very difficult and costly.

From these findings it was concluded that industrial reuse will not be a feasible proposition if large volumes of reclaimed water are to be reused.

A notable exception as far as industrial reuse is concerned is the Athlone power station which is using treated effluent from the Athlone Sewage Works as cooling water. The average volume used is about $3,5 \times 10^6 \text{ m}^3/\text{a}$.

Irrigation Reuse

Substantial volumes of water are allocated for irrigation purposes in the Western Cape. Consequently the use of reclaimed water as a substitute for fresh water which could then be made available for municipal supplies seems to be a feasible reuse option. The various factors which should be considered in this regard include aspects such as the effects of relatively high total dissolved solids (TDS) on production and soil conditions, the cost of reclamation and pumping of reclaimed water to irrigation areas and the acceptance by farmers of reclaimed water to substitute fresh water.

The feasibility of this reuse route as an alternative option for the use of reclaimed water will receive further attention.

CONCLUSION

The fresh water resources available to Cape Town are limited. Projections of water demand indicate that these resources will be fully committed towards the middle of the 1990's. Resort will then have to be taken to unconventional resources to meet further increases in demand. Reclamation of water for recycling in the municipal supply could play an important role in this regard.

The successful diversion of industrial effluents from sewage of domestic origin and the construction of modern regional sewage purification works are important achievements in the long term planning for full scale water recycling. The operation of the prototype demonstration water reclamation plant will be the final and perhaps most important stage in the development of this future water resource for Cape Town

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Table I. Water Sources for Cape Town Supply Area

<u>Source</u>	<u>Assured yield x10⁶m³/a</u>
Dams on Table Mountain	5
Steenbras Dam	38
Wemmershoek Dam	46
Voëlvlei Dam	67
Wellington (local sources)	1
Paarl (local sources)	1
Stellenbosch (local sources)	6
Strand (local sources)	2
	<u>166</u>

Table II. Projected Water Demand for Cape Town Supply Area

<u>Year</u>	<u>Projected demand x10⁶m³/a</u>
1985	260
1990	350
1995	470
2000	632
2005	851

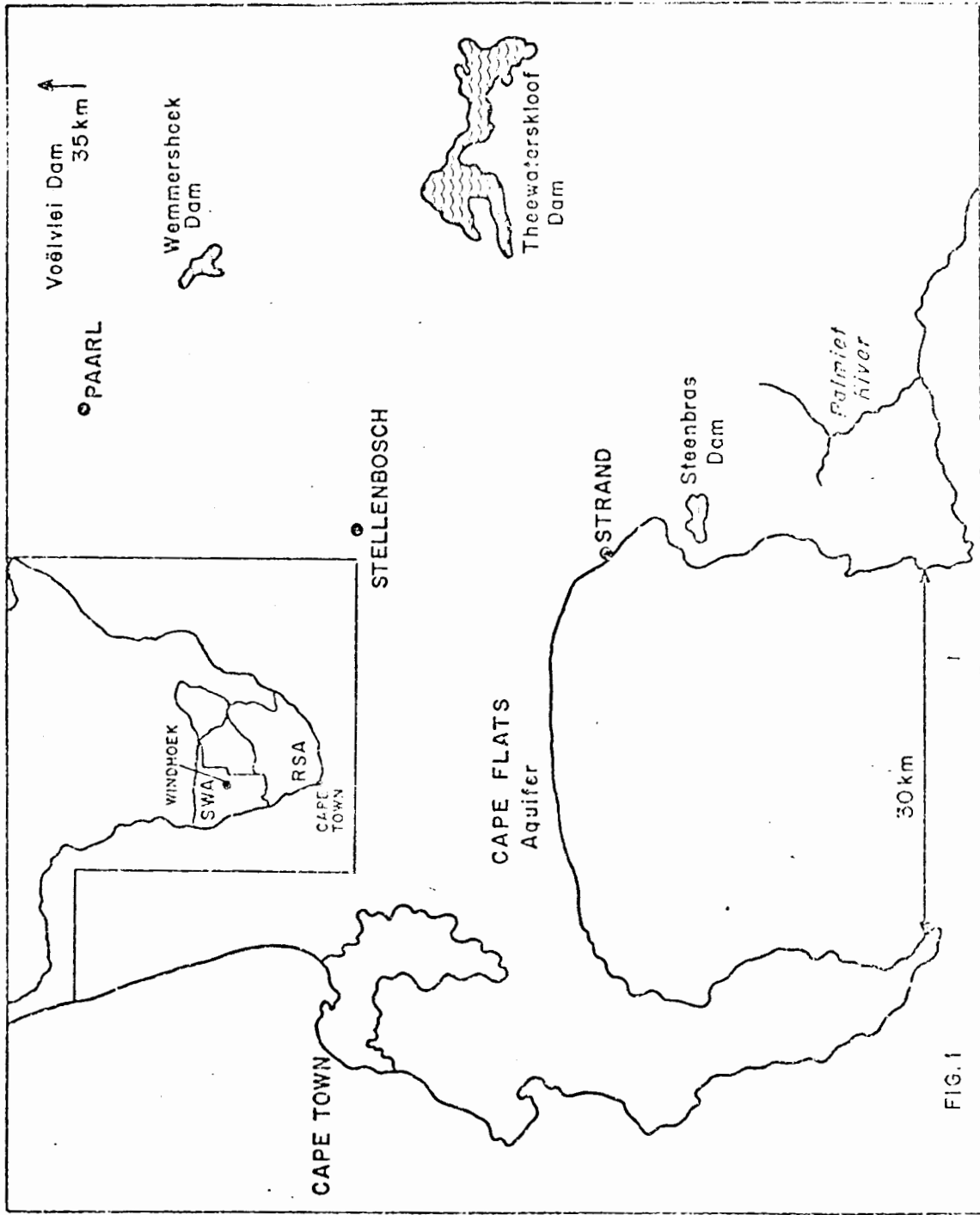


FIG.1

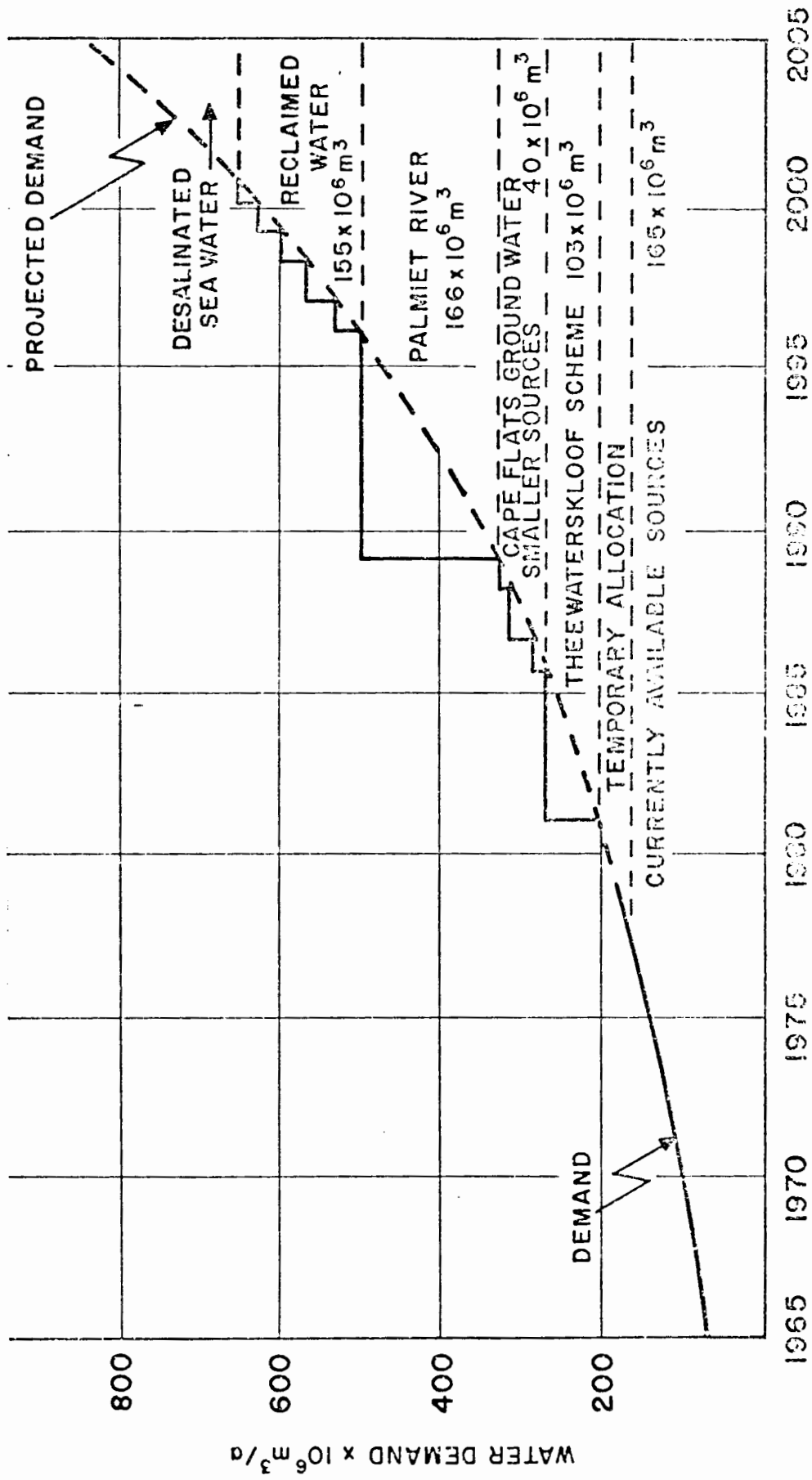
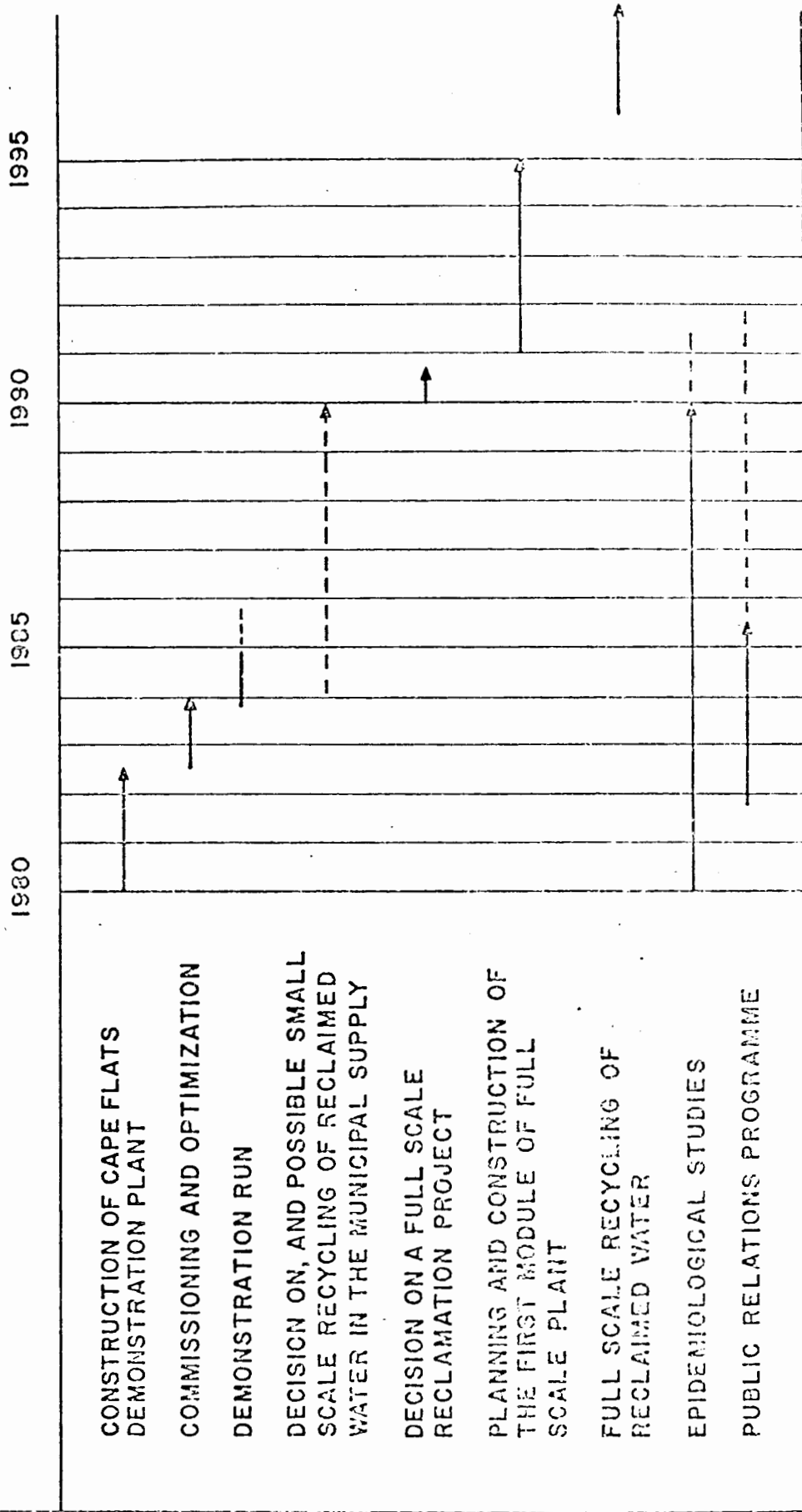


FIG. 2 WATER DEMAND AND PROPOSED DEVELOPMENT OF WATER SOURCES FOR GREATER CAPE TOWN

FIGURE 3

POSSIBLE TIME SCHEDULE FOR THE IMPLEMENTATION OF FULL SCALE RECYCLING OF RECLAIMED WATER IN CAPE TOWN



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WATER RECYCLING FOR DOMESTIC AND AGRICULTURAL APPLICATIONS: STATE OF THE ART

C. F. Schutte

*Senior Adviser, Water Research Commission, P O Box 824,
Pretoria, South Africa*

ABSTRACT

The state of the art of water recycling for domestic (and agricultural) applications is reviewed. Indirect reuse, indirect recycling and direct recycling of water in domestic supplies are discussed with regard to engineering, public health and quality aspects. It is indicated that there is very little difference between indirect reuse of water containing effluents and recycling of reclaimed water for domestic applications. The most important consideration in all reuse situations is that a polluted source is used for the production of drinking water. Quality criteria are therefore required for drinking waters derived from polluted sources (or regardless of source). "Proposed Directives for the Reclamation of Treated Effluents for Direct Recycling and Reuse as Domestic Water" formulated by the South African Department of Health, Welfare and Pensions are given as an Annexure to this paper.

KEYWORDS

Water recycling; water reuse; domestic applications; agricultural applications; public health aspects; planning and engineering aspects; public attitudes.

INTRODUCTION

The terms reclamation, recycling and reuse are in very general use in our contemporary water literature. Yet only a decade or two ago these words were almost non-existent in the vocabulary of water researchers, planners and managers. Today these concepts are being promoted by institutions such as the Office for Water Recycling in California U S A, The Water Reuse Promotion Centre in Japan and state departments in countries such as Israel and South Africa. In addition many millions are being spent on reuse related research in countries including Germany, the United Kingdom and Holland which are not "water short" countries, but where indirect reuse takes place on a large scale. In the past few months two international conferences directed specifically at water reuse were held, viz. Water Reuse Symposium II, and the International Congress on Desalination and Water Reuse, and also at this conference a part of the programme is directed at water recycling.

These examples serve to illustrate the rapid development of the concept of water

recycling and the tremendous growth in research in this field. We have come to realize that reclamation and reuse are important tools in the effective management and utilization of water resources, that the indirect reuse of water which has been accepted unquestioned for many years has serious inherent shortcomings, that improved quality criteria are needed for our domestic water supplies and that we are indeed and have been practicing water recycling in our domestic supplies for many years.

The result of the awareness of these problems is a general increased research effort on aspects directly and indirectly related to water recycling, aimed at ensuring sufficient water supplies of a suitable quality for our water needs. The research efforts cover aspects such as resources management, sewage purification technology, advanced wastewater treatment technology, advanced water treatment technology, desalination technology, analytical techniques, toxicology and epidemiology. With this input into reuse related research it would not be far-fetched to predict that before the turn of the century recycling of water for domestic applications could become a well accepted practice.

Since the concepts of water recycling and reuse are relatively new, reuse terminology is still somewhat unclear. The same word or expression is often used to indicate different concepts and vice versa. There have been many attempts to define concepts in precise terms but all these definitions have to some extent been arbitrary. In this paper the term "recycle" will be used in relation to the process of purification and reticulation of reclaimed water, and "reuse" specifically to those aspects related to the application of reclaimed water. "Reclaimed water" is treated water produced from sewage effluents for a specific reuse application.

This paper deals with the state of the art of water recycling for domestic and agricultural applications. Other presentations in this session on water recycling deal with aspects closely related to this presentation e.g. public acceptability of reclaimed water; water recycling systems; health risks; research needs. It is therefore inevitable that there will be some overlapping and duplication - this may in fact be useful since one could then judge and evaluate the views of the different experts on the same issues.

WATER RECYCLING FOR DOMESTIC APPLICATIONS

Recycling Systems

Two possibilities exist to recycle water for domestic purposes: either in the normal municipal supply in admixture with water from conventional supplies, or in a separate reticulation system for uses such as toilet flushing. Separate reticulation systems will only be feasible within large complexes where relatively large volumes of water are used for domestic applications where potable water is not required. A project of this nature is being developed in a large public housing development in Hong Kong where reclaimed water will be supplied for toilet flushing (To-Hin Lau, 1979). The separate reticulation of reclaimed water for certain domestic applications will be limited to relatively small volumes compared to other possibilities for recycling, and this avenue of recycling will not be discussed further.

Recycling of reclaimed water in the normal municipal supply implies making reclaimed water available for unrestricted use and can take place in different ways: firstly by direct recycling of reclaimed water, i.e. reclamation of water from effluents and direct introduction into the supply system. Secondly, by indirect recycling, comprising the reclamation of water from effluents, discharge of reclaimed water

into a water body which is being used as a drinking water supply source. Thirdly, purified effluents are also used for domestic applications in the form of indirect reuse (or unintentional recycling) as a result of the fact that the same water body is used for discharge of effluents and as a source for water supply.

There are apparent differences between the three concepts mentioned above; direct and indirect recycling being the deliberate and planned reclamation and recycling of water from effluents to increase the water supply, and indirect reuse being the unplanned use of effluents from up-stream dischargers. Further, indirect recycling is a concept very similar to indirect reuse i.e. the reclaimed water is passed through a natural cycle - whereas this is not the case in direct recycling (indirect recycling has also been termed "simulated indirect reuse"). The effect of this difference between direct and indirect recycling is that indirect recycling is more readily accepted by water purveyors, scientists and public health officials. However, the three systems are identical with respect to the main feature, i.e. that water derived from effluents is supplied as domestic water to the user. In effect this means that it should make no difference to the user whether the water supplied is recycled directly, indirectly or unintentionally, provided it is of acceptable quality. The latter system has been accepted as normal practice, therefore, from the users' point of view recycling should also be acceptable. However, this is not the case and doubt is still being expressed by many people, including scientists and health officials, as to the safety of using recycled water for drinking purposes.

This anomaly between the attitude towards indirect reuse vs recycling has been compared to civil vs military justice: Indirect reuse - innocent until proven guilty and recycling - guilty until proven innocent (Heaton, 1981).

A realistic approach to the question of recycling and reuse should be sought in an approach that all these supplies actually comprise the production of water from polluted sources and the same strategies and safety measures and margins should be implemented in all such cases.

Indirect Reuse of Effluents (Unintentional Recycling). This form of reuse is often called unplanned or unintentional or covert reuse because it does not constitute the "deliberate" recycling of water in the municipal supply. Reuse is an inevitable result of the established system where the same river or water body is being used both for disposal of purified effluents and as a water source. In these cases recycling is not in the first place aimed at increasing the water supply but rather is a result of the disposal system (although in many cases downstream users have become dependant on discharges for sufficient supplies). Indirect reuse takes place along most rivers with the Rhine, Seine, Meuse, Mississippi typical examples where purified effluents from cities and industrial complexes are discharged into the river while downstream users depend on it as water source.

This practice of indirect reuse has been accepted for many years under the belief that "natural" purification would render pollutants harmless and that a safe water will be produced through conventional treatment processes. As long as the capacities of biological processes, dissipation and dilution were not overtaxed these processes could indeed produce water of acceptable quality. However as a result of increased industrialization and the continuous development of new chemicals, conventional treatment processes could not cope with the increased loads and advances in analytical techniques have made it possible to detect numerous chemical substances from industrial origin in drinking waters in very small concentrations. Some of these substances are suspected of being toxic and could present health risks to consumers. One solution to this problem of using polluted water as raw water source is to upgrade water treatment works (where alternative unpolluted supplies are not available). The practice in countries such as Germany and Holland is to apply extended water treatment processes including chemical clarification, activated carbon adsorption, and the use of ozone and chlorine dioxide. In

In addition the water is either abstracted as groundwater after river bank filtration or infiltrated into dune or ground aquifers after some form of pretreatment. Several advantages are obtained through ground filtration, including enhanced biological removal of dissolved organic material, removal of microorganisms, and extreme fluctuations in water temperature and quality are evened out. After a long passage which could be for periods varying from a few days to several weeks the water is abstracted in admixture with ground water and undergoes final treatment.

Another approach may be followed where the same authority which is responsible for water supply also has control over effluent discharges. Extensive discharge control measures could be implemented as is done by the Thames Water Authority for the River Lea (Wood and Richardson, 1980). A system of "catchment quality control" or effluent discharge control has been developed to control discharges of effluents containing substances which are suspected of being toxic and non-removable in the treatment system. The first step in such a control strategy is to conduct a complete survey of all discharges and of specific compounds which are used or produced in the catchment area. Those suspected of being toxic and non-removable or non-degradable are identified and mass balances are drawn up and the concentrations monitored throughout the river and treatment works. If found necessary, the final step is to provide special disposal facilities to prevent unwanted substances from entering the sewerage system and thus also the water supply source.

Indirect Recycling. Indirect recycling constitutes the reclaiming of water from effluents and the deliberate and planned discharge of the reclaimed water to a water body which is being used as water supply source in order to increase the volume of water available for abstraction. Indirect recycling can be done via rivers, impoundments or lakes, or via infiltration into groundwater.

With indirect recycling, standards can be set to which the reclaimed water must comply before being introduced into the water supply source and measures such as effluent discharge control as described above can be introduced to protect water supplies.

The most acceptable way of recycling is via infiltration to supplement ground water supplies where a suitable aquifer exist (Roberts, 1980). The filtration action and biological activity in the soil together with dilution and retention in the aquifer ensures that a water of potable quality would be produced after final treatment. Ground water can be recharged by infiltration of reclaimed water or by deep well injection. Infiltration comprises spreading of reclaimed water and percolation of the water down into the aquifer with further improvement in quality taking place as a result of the filtration action of the soil and micro-biological action. Deep well injection does not afford any further improvement in water quality as does infiltration and the quality of injected water should therefore be comparable to that of the ground water.

Indirect recycling has the following features which make it more readily acceptable than direct recycling to the public and to public health authorities: its similarity to indirect reuse which has been taking place for many years, the loss of the effluent identity when reclaimed water is discharged to a water body, the time lapse and distance between the time and point of discharge and the time and point of abstraction, continued biological activity and dissipation which result in improved quality and quality attenuation as a result of dilution with the water body.

Certain other considerations such as the possibility of pollution of reclaimed water through other discharges into the water body or as a result of eutrophication in a surface water body must also be considered as well as evaporation, evapotranspiration and seepage losses which might make indirect recycling economically less attractive.

A large number of projects exists where water is recycled indirectly. The systems include the infiltration of secondary treated effluents into aquifers e.g. Montebello Forebay region, Los Angeles U S A, the injection of very highly treated reclaimed water through deep well injection into aquifers e.g. Water Factory 21 and the discharge of reclaimed water into surface water bodies e.g. from the Upper Occoquan WWT Plant into the water supply source for Fairfax, U S A.

Direct Recycling. Direct recycling comprises reclamation of water to potable quality and direct introduction into the reticulation system in admixture with water from other sources. Windhoek, S W A is the only city practising this form of recycling (Van Vuuren, Clayton and Van der Post, 1980). The plant has been in intermittent operation since 1969 and is only relied upon to supplement the normal supply to the city when conventional supplies fall short. The capacity is 4500 m³/day and constitutes an average about twenty percent of the particular supply into which the reclaimed water is introduced.

The whole operation is intensively monitored through surveillance of reclaimed as well as other supply water quality, epidemiological surveys of the population as a whole as well as a biological monitoring system. There have been no indications of any adverse effects due to the use of reclaimed water (Isaacson, 1981).

The system comprises biological purification of sewage from essentially domestic origin in an activated sludge plant designed to remove phosphates and nitrogen biologically. The plant produces an effluent with an NH₃-N concentration of less than 1 mg/l. After biological purification the effluent passes through a system of maturation ponds with a retention time of approximately twelve days and flows a distance of several kilometers before being reclaimed in a plant consisting of chemical clarification, sandfiltration, break point chlorination, activated carbon adsorption and final chlorination. It is then mixed with purified water from a conventional source and distributed.

Public Health Aspects

A prerequisite for the recycling of water for domestic applications is that the reclaimed water must be safe for human consumption. The definition of "safe" with regard to micro-biological quality and the permissible concentration of inorganic and certain organic substances does not present a problem since standards already exist. However, the question of what is "safe" for organic micro pollutants is not so readily answered. In view of the fact that it is not possible to fully analyse dissolved organic matter in water and since reclaimed water is derived from a polluted source there could be substances present in micro- or even nano-quantities which might present a health risk, however small such a risk may be. It could be stated therefore that "safe" is qualified by the degree of risk involved in the drinking of reclaimed water (or any other water or in taking any other action). Therefore if it can be shown that there is no more risk involved in drinking reclaimed water than in drinking water from conventional supplies then there is no reason why reclaimed water should not be acceptable as a water supply for a particular area. This could be done by analysing a reclaimed water as completely as possible and to test it for mutagenicity, carcinogenicity and all other possible effects and to compare these findings to those obtained on conventional water supplies for the area. In addition it must be guaranteed that safety measures are incorporated in a recycle system to ensure that no "sub standard" water will be recycled.

However, this relative approach is not entirely satisfactory because the quality of conventional supplies which are used as reference could be open to question. An absolute reference quality should be established and therefore the only real solu-

tion would be to develop a set of criteria for drinking water regardless of source - which should therefore also apply to reclaimed water. This approach was advocated by many of the delegates to the USEPA workshop on "Protocol Development : Criteria and Standards for Potable Reuse and Feasible Alternatives" held during July 1980. In addition to defining quality criteria for drinking water, regardless of source, or until such time as such criteria have been developed health authorities should also prescribe additional requirements with respect to the recycling operation as a whole to ensure that the drinking water supplied will not result in any undue health risk to the consumer. Such requirements for the recharge of aquifers have been set by the State of California (State Health Department, California, 1978), and tentative guidelines for potable reuse have been developed for Israel (Shelef, 1980).

A significant development with regard to potable reuse is the publication by the South African Department of Health, Welfare and Pensions of "Proposed Directives for the Reclamation of Treated Effluents for Direct Recycling and Reuse as Domestic Water". These directives will be used to evaluate the merits of proposed projects for recycling on a case by case basis. The Annexure to this paper gives the proposed directives.

Epidemiological Evidence

The difficulties in fully analysing drinking waters and the uncertainties with respect to health implications of micro pollutants in water supplies have been pointed out above. A strategy which could give an answer in retrospect to questions regarding safety of drinking waters is to conduct epidemiologic surveys and studies on populations that have been receiving reclaimed water. However, the process of obtaining epidemiologic answers to these questions is also fraught with problems. Since only minor health effects or effects over relatively long periods of time can be expected, if such effects would indeed occur, the main problems are firstly, to identify subtle changes in the health pattern of a community against the natural background of changes in health patterns, and secondly to isolate any effects due to water usage from effects due to socio-economic or other factors such as dietary, drinking and smoking habits.

A number of epidemiologic studies related to water usage have been reported. Most of these studies have been conducted on communities exposed to indirect reuse and specifically to high concentrations of chloroform in water supplies compared to supplies with low concentrations, or to surface water compared to ground water, or chlorinated vs unchlorinated supplies.

Epidemiologic studies have been conducted at two projects where water is recycled, viz. Montebello Forebay in Los Angeles where water is recycled indirectly via infiltration and Windhoek where water is recycled directly. Since the early 1960's the local groundwater supplies in Montebello Forebay have been supplemented by the infiltration of secondary treated effluents. The first report on the epidemiologic study covers the period 1969-1971 and concludes that "there were no grossly apparent adverse health effects associated with the use of recycled water" (Frerichs, Satin and Sloss, 1981). The study is continuing for the period 1972-1978 along the same lines as the one reported. In addition, surveys on more sensitive health indicators are being planned.

According to findings on the Windhoek project (Isaacson, 1978) no meaningful increases in the occurrence of infectious diseases could be detected in areas where and during periods when water was recycled compared to areas which were not supplied with reclaimed water. As far as chronic non-communicable diseases are concerned no analysis has been performed since insufficient morbidity and mortality data is

available at this stage.

A similar study has recently been launched in Cape Town, South Africa (Bourne and Watermeyer, 1981). In view of the fact that reclaimed water might be recycled in the municipal supply in future the present study is aimed at obtaining background data against which future data may be compared should recycling of water become a reality.

Planning and Engineering Aspects

Any project for the recycling of water in the municipal supply will be a result of existing or projected deficits in water supply to that area. It is obvious that all alternatives to meet projected demands should be evaluated. In water short areas where all available conventional supplies have been fully committed there may be one or more of the following alternatives: transportation of water from distant sources; recycling of reclaimed water; desalination of brackish or sea water. The economics of the different possible schemes will to a large extent be a deciding factor as to which alternative will be the most feasible for making additional water available. The one alternative which will usually be feasible is the recycling of reclaimed water.

In order to determine the most feasible application of reclaimed water, potential markets for reclaimed water should be surveyed. Broadly speaking the potential market for recycling can be divided into three basic categories viz.:

- (i) Irrigation, which usually accounts for the greatest abstraction of fresh water in water short countries (50-80% of the total abstractions). Limitations to this potential reuse market are the geographic location of irrigation schemes relative to the reclaimed water source; effect of relatively high loads of mineral salts particularly Na^+ and Cl^- on crop production; the fact that in many cases irrigation farmers already rely on indirect reuse of effluents for their irrigation needs. Reclaimed water is particularly useful for replacing fresh water for irrigation of parks, golf courses and green belt areas.
- (ii) Industry including power plants: This sector also represents a large abstraction of fresh water supplies particularly for cooling purposes and could well utilize reclaimed water. The following factors could affect reuse: Cost of reticulation of reclaimed water unless demands are sufficiently large and confined in specific areas; higher dissolved salts in reclaimed water could necessitate larger intake volumes or less internal recycling.
- (iii) Municipal supplies usually represent only a relatively small fraction of total fresh water abstraction. However, the demand for municipal supplies is ever increasing and additional supplies must continuously be found. Reclaimed water is one source that will always be available to satisfy part of increases in demand. From a supply/demand point of view the use of reclaimed water in the municipal supply will be a feasible proposition to make relatively large volumes of additional water available. In certain water short areas therefore the recycling of reclaimed water in the municipal supply might be the only solution to make additional water available to satisfy increases in demand. Full scale projects to recycle water in the municipal supply are usually preceded by research and small scale demonstration projects to establish criteria for design and operation for full

operations since these criteria are inter alia, determined by feed water quality which may vary from place to place.

Reclamation Technology

The state-of-the-art with respect to reclamation technology is such that water of just about any desired quality can be produced by linking different treatment processes. However, every additional process has cost implications (cost figures for different levels of treatment are available (Culp/Wesner/Culp)) and the unnecessary inclusion of processes might result in such high production costs that reclamation becomes unfeasible altogether. It is therefore essential that realistic requirements be set for the process as such - without compromising quality.

A large number of research projects are in progress on aspects such as the application and efficacy of active carbon adsorption, ozone, chlorine dioxide, air stripping and combinations of processes to reduce the organic content and specified groups of compounds such as total organic chlorine in reclaimed water as far as possible. Further improvements in the efficacy of these processes could be expected especially if analytical technology develops sufficiently to enable full analysis of the organic matter in water to be made.

The inorganic salts in reclaimed water do not present a health hazard. However in a closed recycle system there will be a continuous build up of inorganic salts unless some form of desalination is incorporated in the treatment train. The increase in dissolved solids in the water reaching the consumer will be determined by the recycle rate and the dissolved solids concentration in the reclaimed water relative to that of the fresh water supply. An analysis of increases in total dissolved solids under different conditions shows that in areas with a relatively low TDS fresh water supply and a recycle rate of less than say 30%, desalination need not be a requirement. However, from the point of view that reverse osmosis is a very effective process for removal of colloidal matter and of dissolved organics of higher molecular mass it may be feasible to incorporate reverse osmosis into a treatment train thus getting the benefit of desalinated water in addition to water with a very low organic content. A number of research projects on the efficacy and application of reverse osmosis for water reclamation and in particular on pretreatment of water to prevent membrane fouling and flux decline are in progress. Reverse osmosis is applied on full scale (1900 m³/day) at Water Factory 21 to desalinate reclaimed water before injection into an aquifer (Argo, 1979).

Public attitudes

Public attitudes towards water recycling for domestic applications are influenced primarily by concerns about the safety of water supplies containing recycled water. Reassurances regarding safety could only be given by scientists, engineers and health officials. In the final instance therefore the public attitude towards water recycling will to a large extent be a reflection of the professional and personal biases and attitudes of the scientific community. If they are reassured about the safety of a water supply whether reused indirectly, recycled directly or indirectly this feeling will be passed on to the public making the public positively inclined to recycling.

Another aspect which might influence public attitudes is the psychological repugnance associated with the idea of drinking water derived from wastewater. This misconception could be overcome by informing the public about the true state of affairs regarding quality.

A number of surveys to assess public attitudes towards water recycling have been reported (Bruwold and Crook, 1980). Results from these studies indicate that there is neither a decisive negative nor positive inclination towards recycling for drinking purposes although most studies did indicate that the majority of people interviewed were not in favour of recycling for drinking purposes.

The general conclusions from these surveys are that the majority of people interviewed want water recycling options that will protect public health, conserve water and preserve the environment. Further that younger, more educated, more affluent people will more readily accept recycling in drinking water than will older, less educated, less affluent people.

It would appear that public acceptance of water recycling will not be a major obstacle in development of water reuse projects provided that well designed and well conducted public information programmes are launched in good time.

WATER RECYCLING FOR AGRICULTURAL APPLICATIONS

Recycling of water for agricultural applications is a very old practice dating back to ancient times. In more recent times (18th-19th century) sewage farming was general practice in Europe, the U S A and the U K. These forms of reuse were not recycling in the true sense of the word but rather sewage disposal.

In modern times many irrigation projects rely heavily on effluent discharges to rivers or dams to ensure sufficient supplies for irrigation needs. Direct recycling of effluents for irrigation, including irrigation of parks, golf courses and green lands, has also become an accepted practice in many parts of the world.

Two aspects are of concern as far as water quality is concerned. Firstly, public health aspects due to contact between the public and irrigation water and consumption of food that has been irrigated with reclaimed water, and secondly possible effects on crop production as a result of water quality especially with regard to dissolved inorganic salts.

Quality requirements with regard to the first aspect have been published inter alia by South Africa (RSA Department of Health, 1978), the State of California (State Health Department, California, 1978) and Israel (Shelef, 1981). These requirements in general stipulate treatment and quality requirements for various types of crops ranging from those eaten raw for which highly treated irrigation water is required to the irrigation of fibrous fodder material for which only limited treatment is required.

Effects on crop production as a result of irrigation water quality are mainly due to high concentrations of dissolved inorganic salts such as sodium, chloride and boron. Sodium affects the sodium absorption ratio while high concentrations of chloride are detrimental to tobacco production, for example. Since the type of soil, the type of crop grown and the irrigation rate are all important factors, every project must be evaluated individually.

The following factors related to the reticulation of reclaimed water should also be considered. Since a separate reticulation system is required special precautions must be taken to prevent any possibility of cross connections with the municipal supply. The possibility of slime formation within the reticulation system and suspended solids causing blocking especially in drip irrigation systems should be kept in mind.

CONCLUSION

Indirect reuse of water for domestic applications has been in general practice for many years. Recent concerns about the quality of indirectly reused water have resulted in treatment processes being upgraded, in the application of discharge control in catchment areas and in an acceleration of, and intensification in research related to drinking water quality and process improvement. As a result of these efforts additional and more stringent quality criteria have been set. However, the process has not been completed and efforts are continuing.

Recycling of water in the municipal supply is practiced in a relatively small number of locations - Windhoek being the only place where water is recycled directly, with Whittier Narrows, Water Factory 21, Upper Occoquan and Long Island all in the U S A examples of indirect recycling.

A point which should be realized and accepted by health officials and the scientific and engineering community is that there is in the final analysis very little difference between indirect reuse of water derived from effluents, and recycling of reclaimed water in the municipal supply. These systems should all be regarded as producing water from polluted sources. High priority should therefore be given to the development of a set of quality standards for drinking waters derived from polluted sources (or for that matter irrespective of source). The EPA has initiated the process in the U S A by organization of the Airlie workshop on protocol development while the South African Department of Health, Welfare and Pensions has published proposed directives for the recycling of water for domestic applications.

Treatment technology does not seem to present a limiting factor in the implementation of water recycling. Research in this field is however continuing and further improvements can be expected in the future.

Public support for any project to recycle water in the municipal supply is of vital importance and here again indications are that the public attitude will be favourable if a timely start is made with public information and demonstration programmes.

Current recycling projects comprising advanced reclamation technology are performing exceptionally well if judged by the quality of water that is being produced. It can only be hoped that results from research on quality parameters, toxicology and epidemiology will become available in the near future to allay the apprehensions which are still evident in parts of the scientific community towards water recycling.

As regards agricultural applications it can be stated that recycling of reclaimed water for irrigation of crops and green land areas is a very successful way of utilizing existing water supplies to its maximum or to replace fresh water supplies which could be better utilized for domestic and industrial applications.

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REJECTION OF ALKYL PHENOLS BY REVERSE OSMOSIS MEMBRANES

C Frik Schutte* and Georges Belfort**

*Water Research Commission, P O Box 824, Pretoria 0001, RSA

**Dept of Chemical and Environmental Engineering, Rensselaer Polytechnic Institute, TROY, NY 12181, USA

ABSTRACT

The removal of different alkyl phenols by two commercially available reverse osmosis membranes, one cellulose acetate and one aromatic polyamide both with very high rejection of NaCl was investigated. The polyamide membrane rejected phenol very effectively while the cellulose acetate membrane showed virtually no phenol retention. In order to explain these differences a study was made of the mechanisms of phenol rejection by the two membranes. Transient diffusion tests as well as partitioning tests were conducted in addition to the reverse osmosis experiments. From the results it is concluded that phenol is sorbed in both membranes and that the forces of attraction between phenol and cellulose acetate are relatively weak compared to the attraction between phenol and polyamide resulting in a faster rate of diffusion in cellulose acetate and hence poor rejection.

KEYWORDS

Reverse osmosis, phenol, cellulose acetate, aromatic polyamide, membranes, sorption, diffusion.

INTRODUCTION

Phenol and phenolic compounds are present in many industrial wastewaters especially from coal based and other chemical and petro-chemical industries (Lamb *et al.*, 1979). Phenol is toxic and must therefore be removed to very low concentrations before these wastewaters can be discharged. With the growing interest in the application of reverse osmosis for industrial wastewater treatment and for water reclamation and recycling it is important that data should be available on the rejection of phenol by membranes and on factors affecting rejection.

Different studies have shown phenol to be poorly rejected by cellulose acetate membranes and that in some cases it may even permeate membranes preferentially to water. Matsuura and Sourirajan (1971) found rejections of +1% and -2% respectively for two cellulose acetate membranes at 1700 kPa and 25°C. They also studied the removal of a series of alcohols and concluded that alcohols are better separated than phenol because alcohols have less hydrogen bonding ability than phenol as expressed by the relative acidity of the molecule.

Matsuura *et al.* (1974) studied the separation of phenols by aromatic polyamide membranes and concluded that the positive separation by polyamide membranes is due to the preferential sorption of solute at the membrane-solution interface caused by both the non-polar character of the membrane and the acidity of the solute.

In a study on the rejection of a group of low molecular mass organics by five different membranes Chian and Fang (1976) found different patterns of removal of organics by cellulose acetate and by polyamide membranes. For the group of organics in general and for phenol in particular they found very good removal by the polyamide membranes and relatively poor removal by the cellulose acetate membranes. They concluded that polar together with steric effects play a major role in the rejection of solutes with the same functional group for all membrane materials.

Jonsson (1978) used different membrane models to determine the intrinsic membrane rejection, R_{\max} for different solutes. He found asymptotic R_{\max} values at high pressures of ~45% for phenol and cellulose acetate membranes.

Nakagawa *et al.* (1984) reported on the rejection of organics by the composite PEC 1000 membrane, in which the active membrane layer is prepared from cross-linked polyether. This membrane has excellent rejection properties with respect to dissolved organics e.g. ethanol 97%, acetic acid 86% and phenol 99,0% at 5600 kPa and 25°C.

In this study the rejection of phenol by a cellulose acetate and a composite aromatic polyamide membrane was investigated. In order to better understand the different mechanisms of removal by these membranes two series of tests in addition to the reverse osmosis experiments were conducted i.e. a series of transient phenol diffusion tests and a series of partitioning tests.

THEORETICAL

Solute and solvent flux through a semi-permeable membrane may be represented by models derived from the thermodynamics of irreversible processes such as the model developed by Kedem and Katchalsky (1958) :

$$J_v = L_p (\Delta P - \sigma \Delta \pi) \text{ for solvent flux and } \quad (1)$$

$$J_s = (C_s) \ln(1 - \sigma) J_v + \omega \Delta \pi \text{ for solute flux} \quad (2)$$

Solute rejection is defined as $R = 1 - C_p/C_{fw}$ (3)

and if $C_p = J_s/(J_s + J_w)$ then (4)

$$R = 1 - J_s/(J_s + J_w) C_{fw} \quad (5)$$

now solvent flux can also be given by

$$J_s = \omega (C_{fw} - C_p) = \omega C_{fw} \text{ and } J_v = (J_s + J_w) \quad (6)$$

substituting (6) and (1) into (5) gives

$$1 - R = [C_{fw} + L_p/\omega (\Delta P - \sigma \Delta \pi)]^{-1} \quad (7)$$

if $C_{fw} = C_o (1 + R/(1-R))$ then

$$1/(1 - R) = C_o [1 + R/(1-R)] + L_p/\omega (\Delta P - \sigma \Delta \pi)$$

$$1/(1 - R) = C_o/(1-R) + L_p/\omega (\Delta P - \sigma \Delta \pi)$$

$$\begin{aligned} 1/(1 - R) - C_o/(1 - R) &= L_p/\omega (\Delta P - \sigma \Delta \pi) \\ 1/(1 - R) [1 - C_o] &= L_p/\omega (\Delta P - \sigma \Delta \pi) \end{aligned} \quad (8)$$

Thus, by plotting $(1 - R)$ vs $(\Delta P - \sigma \Delta \pi)$ the slope gives $(1 - C_o)/L_p$ from which ω may be obtained, where $\omega = (C_s) \ln(L_D L_p - L_{pD}^2)/L_p$, the coefficient of solute permeability.

An alternative relationship between R and J_v was developed by Pusch (1977)

$$1/R = 1/R_x + (L_D/L_p - R_x^2) L_p \Pi_R / R_x J_v \quad (9)$$

or
$$1/R = 1/R_x + (L_D/L_p - \sigma^2) (1 - R_x)/(1 - \sigma) 1/J_v \quad (10)$$

Therefore, a plot of $1/R$ versus $1/J_v$ should give a straight line with a slope of $(L_D/L_p - \sigma^2)(1 - R_x)/(1 - \sigma)$ and an intercept of $1/R_x$. As J_v becomes increasingly large, at large ΔP , the rejection reaches an asymptotic value of R_x , which is a well known phenomenon in reverse osmosis processes.

EXPERIMENTAL

Membranes

The following membranes were used in this study :

- (i) A composite membrane (FT-30, Filmtec Corp. Mn.) consisting of a very dense cross linked aromatic polyamide skin of 0.2μ thickness on a 35μ polysulphone support membrane.
- (ii) A polysulphone membrane used as the support for the FT-30 composite membrane.
- (iii) An asymmetric cellulose acetate membrane with a high NaCl rejection (SEPA 99, Osmonics Inc., Mn.).

Reverse osmosis test unit and procedures

The test unit was equipped with four stainless steel high pressure test cells which could be operated in series or either one or more could be bypassed. The test cells were 48 mm in diameter and flow was across the membranes. The flow rate could be controlled at between 0.5 and 8 l/min and the unit could be operated at steady operating pressures in the range 550 - 6900 kPa (80-1000 psi). Operation was in a recycle mode, i.e. the feed-reject solution as well as permeate were recycled to a plastic feed reservoir. Samples of feed and product were taken at regular intervals but the volume of samples were small (50 ml) compared to the total volume in the system (about 100 l). Since the performance of the membranes is affected by the "history" of operation, the same procedure was followed in all the experiments. All new membranes were at the start of a run "stabilized" by operating with pure water (de-ionised, ultra filtered 10 000 Daltons) at 5516 kPa for 3 hours. After this stabilization or compaction period pure water fluxes were determined at different pressures (usually in descending order) of 5516, 4137, 2758 and 1379 kPa.

Single solute solutions were prepared by mixing pre-weighed quantities of pure solute (>99.5% purity) in deionised ultrafiltered water in the covered feed tank. Feed samples were taken at the start of a run and at regular intervals during the run to coincide with sampling of permeate and reject. Permeate and reject were continuously recycled to the feed reservoir.

Since heat is added to the feed by the high pressure pump and this is recycled to the feed tank it was necessary to cool the feed reservoir by circulating cooling water through a cooling coil in the feed tank to keep the temperature at $25 \pm 1^\circ\text{C}$.

The unit was operated for at least two hours for equilibrium to be established after any change in the operating conditions i.e. change in operating pressure or change in feed concentration. Membranes were replaced after each run with a particular solute before a new solution was introduced. One of the four test membranes was, however, not replaced, in order to determine the effect of different organics on rejection and flux over an extended period of time.

Partitioning/sorption test procedures

Since the amount of membrane material relative to membrane surface area in reverse osmosis membranes is small and also because the amount of solute sorbed by the membrane materials is relatively small accurate determination of the amounts of organics sorbed is difficult. In order to get as much membrane as possible in contact with a relative small volume of solute long pieces of membrane were rolled and placed in test tubes filled with the solution of interest. Membranes were placed in solutions of different concentrations and the changes in concentration of the solution were monitored until equilibrium was reached.

Some of the membranes contained residual chemicals which gave falsely high readings in initial tests. All the membranes were therefore washed in deionised water until most chemicals were leached out before any sorption tests were initiated.

It was not possible to separate the polyamide skin from the understructure of the composite membrane. The amount sorbed by the skin was therefore determined from the difference between the amounts adsorbed separately by the composite membrane and that sorbed by the polysulphone

understructure.

A second set of tests monitored sorption (and also desorption) independently from both the skin and porous sides of the membranes, when placed in the diffusion cell.

Diffusion test cell and procedures

The diffusion cell consisted of two magnetically mixed chambers (filled volume 41 ml) separated by a membrane (exposed surface area 7.07 cm²) which was held between two spacers. Each chamber was surrounded by two outer chambers through which water was passed for temperature control.

Membranes used in the diffusion tests were also washed in de-ionised water to remove un-reacted chemicals. A circular piece of membrane was placed between the two spacers between the chambers of the diffusion cell. Pure water was put in one chamber and the solution of interest in the other chamber at the skin side of the membrane. The increase in concentration in the pure water chamber was then monitored at intervals of 2 minutes until a steady rate of increase was maintained.

Temperature was controlled at 25 ± 0,25°C.

Solutes

Reverse osmosis data on the following alkyl phenols were obtained : phenol, 4-methylphenol, 4-ethylphenol, 2,6 dimethylphenol, 4-n propylphenol, 4-isopropylphenol.

- Sorption and diffusion tests were conducted with phenol only since the solubility of the other homologues in water is too low and permeation too slow to obtain meaningful data.

Phenol concentrations were determined with a Perkin Elmer spectrophotometer model 552 and sodium chloride concentrations with a Beckman model 39093 conductivity cell.

RESULTS AND DISCUSSION

Characterization tests

In order to relate the organic rejections and volume fluxes of membranes to their performances with sodium chloride, an initial series of characterization tests was done. This included the determination of pure water fluxes under different operating pressures as well as rejections and fluxes with different sodium chloride solutions.

- Pure water permeation rates were determined using stabilized membranes and de-ionised ultrafiltered (10 000 mol.wt. cut-off) feed water.

The small membrane samples used in the test cells showed a relatively large variation in water flux due to irregularities in membrane thickness. The range of fluxes found in this study is shown in Figure 1 (new membranes stabilized at 5516 kPa for 3 hours). The flux of one composite membrane which was in the test cell over a period of 3 months and about 250 hours of operation and which has seen different alcohol and phenol solutions is also shown in Figure 1.

The hydraulic permeability of the membranes calculated from $J_v = L_p (\Delta P - \sigma \Delta \pi)$ (where $\Delta \pi = 0$ for pure water), ranges between

$L_p = 6,44 \times 10^{-7}$ to $7,64 \times 10^{-7}$ cm sec⁻¹ kPa⁻¹ for the FT-30 membrane, and

$L_p = 1,1 \times 10^{-7}$ to $1,46 \times 10^{-7}$ cm sec⁻¹ kPa for the SEPA 99 membrane.

Water flux and rejection data for NaCl feed solutions are summarized in Table 1. Four different feed solutions were used in these experiments (2 500, 10 000, 20 000 and 30 000 mg/l NaCl respectively) at four different pressures. It should be pointed out that at the higher NaCl concentrations fouling of the membranes was caused by corrosion products which could not be removed completely by cartridge filtration.

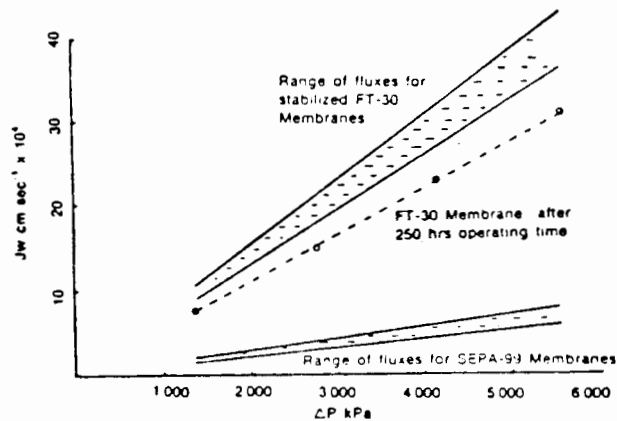


FIGURE 1: PURE WATER FLUX (J_w) vs OPERATING PRESSURE (ΔP)

This is reflected by different L_p values for the same membranes with different solutions.

$$\begin{aligned}
 L_p (2\,500 \text{ mg/l}) &= 6,9 \times 10^{-7} \text{ cm sec}^{-1} \text{ kPa}^{-1} \\
 L_p (10\,000 \text{ mg/l}) &= 6,6 \times 10^{-7} \text{ cm sec}^{-1} \text{ kPa}^{-1} \\
 L_p (20\,000 \text{ mg/l}) &= 5,3 \times 10^{-7} \text{ cm sec}^{-1} \text{ kPa}^{-1} \\
 L_p (30\,000 \text{ mg/l}) &= 3,8 \times 10^{-7} \text{ cm sec}^{-1} \text{ kPa}^{-1} \\
 L_p (\text{pure water}) &= 7,2 \times 10^{-7} \text{ cm sec}^{-1} \text{ kPa}^{-1}
 \end{aligned}$$

TABLE 1: WATER FLUX AND REJECTION DATA FOR NaCl FEED SOLUTIONS AND FT-30 AND SEPA-99 MEMBRANES

FEED CONC	PARAM	MEMBR	PRESSURE ΔP (kPa)			
			5516	4137	2758	1379
2500 ($p = 199 \text{ kPa}$)	R	FT-30	0.995	0.994	0.993	0.983
		SEPA	0.950	0.986	0.979	0.970
	J_v cm/S $\times 10^4$	FT-30	33.0	24.8	16.7	8.5
		SEPA	7.0	5.1	3.5	1.8
10 000 ($p = 793 \text{ kPa}$)	R	FT-30	0.993	0.992	0.986	0.972
	J_v cm/S $\times 10^4$	FT-30	31.2	21.0	12.4	3.9
20 000 ($p = 1\,586 \text{ kPa}$)	R	FT-30	0.994	0.992	0.986	—
	J_v cm/S $\times 10^4$	FT-30	21.2	13.4	6.6	—
30 000 ($p = 2\,379 \text{ kPa}$)	R	FT-30	0.992	0.989	0.981	—
	J_v cm/S $\times 10^4$	FT-30	12.1	7.2	2.1	—

NaCl rejection (R) can be related to solvent flux J_v by equations (8) or (10). Equation (10) gives the asymptotic maximum rejection value, R_x when plotting $1/R$ versus $1/J_v$. Figure 2 shows plots of $1/R$ vs $1/J_v$ for three different NaCl solutions, and these give $R_x = 0,996$; $0,998$ and $0,997$ for 10 000, 20 000 and 30 000 mg/l respectively.

Rejection of alkyl phenols

A summary of the rejection data for the alkyl phenols is given in Table 2.

It is evident from Table 2 that the mechanism of rejection is different for the two types of membranes. Both membranes reject NaCl very efficiently and must therefore be very "tight", yet the cellulose acetate membrane has virtually no rejection of phenol and very low rejection for the higher homologues while the polyamide membrane rejects phenol very effectively.

Rejection of the different alkyl phenols by the FT-30 membrane increases with increasing molecular mass and with increasing hydrodynamic size of the solute molecule. The effect of hydrodynamic size seems to overshadow the effect of molecular mass as can be seen from the rejection of the bulky 2,6 dimethyl phenol molecule with a mol mass of 122,2 compared to the rejection of 4-n propyl phenol with mol mass 136,2. Schutte and Delfort (1985) showed that the rejection of alkyl phenols and alkyl alcohols by the composite FT-30 membrane correlates very well with the corrected cavity surface area of solute molecules ($r^2 = 0,9603$ for the alkyl phenols in Table 2), where corrected cavity surface area is a measure of the hydrodynamic size of the solute molecule.

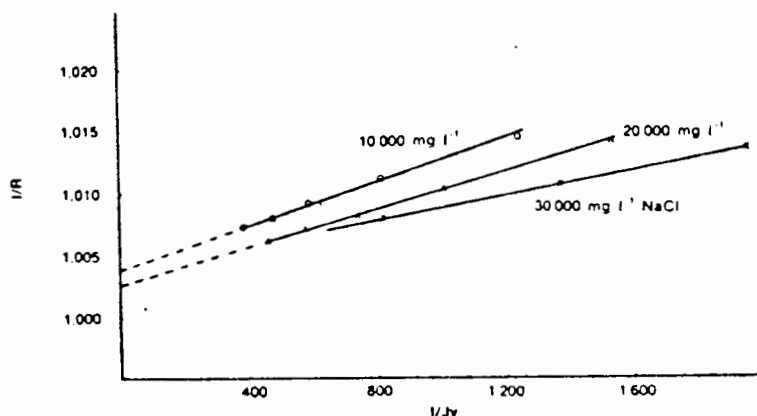


FIGURE 2: $1/J_v$ vs $1/R$, FT-30 MEMBRANE, NaCl

TABLE 2: REVERSE OSMOSIS DATA FOR PHENOLS. DILUTE FEED SOLUTIONS 2,0 mmol l^{-1} 25°C

SOLUTE	FT-30 R at 1 379 kPa	FT-30 R at 2 758 kPa	FT-30 R at 5 516 kPa	Mol wt	SEPA-99 R at 1 379 kPa	SEPA-99 R at 2 758 kPa	SEPA-99 R at 5 516 kPa
Phenol	0.87	0.92	0.94	94.1	0.02	0	-0.04
4 Methyl Phenol	0.91	0.94	0.967	108.1	NA	NA	NA
4 Ethyl Phenol	0.93	0.96	0.970	122.2	NA	NA	NA
2,6 Dimethyl Phenol	0.975	0.978	0.991	122.2	0.44	0.31	0.20
4-n Propyl Phenol	0.967	0.976	0.980	136.2	0.20	0.11	0.05
4 Isopropyl Phenol	0.978	0.984	0.988	136.2	0.38	0.35	0.23

Effect of operating pressure

The effect of operating pressure on phenol rejection is different for the two types of membranes. Rejection by the FT-30 membrane follows the normal pattern of higher rejection with increasing operating pressure, while rejection by the cellulose acetate membrane drops with increasing pressure.

Figure 3 shows this effect for two FT-30 membranes (one new stabilized membrane and the other after 150 hrs of operation) as well as for the SEPA-99 cellulose acetate membrane. Phenol rejection by the polyamide FT-30 membrane follows the classic R vs ΔP pattern in which R asymptotically approaches R_x at operating pressures higher than about 3 000 kPa. The same pattern of rejection is followed for all the different phenols with rejection increasing as the size of the phenol molecule increases.

Figure 4 shows that the model of equation (10) is valid for phenol solutions and the FT-30 membrane. The plots of $1/J_v$ vs $1/R$ are straight lines giving R_x values between 0,962 and 0,971 for solutions of 1,4; 2,5; 21,2; 42,5 and 69,1 mmoles/l respectively.

The situation is, however, different for the cellulose acetate membrane. Rejection of phenol

may be negative at high pressures and the trend is for rejection to decrease as the operating pressure increases. It should also be pointed out that when rejection is poor the reproducibility of data is not very good, so that trends rather than absolute values are important.

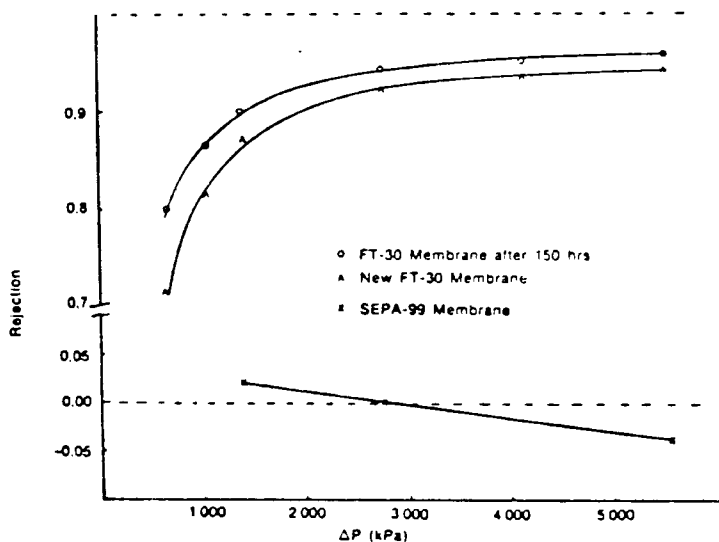


FIGURE 3: REJECTION (R) vs OPERATING PRESSURE (ΔP) FOR DILUTE PHENOL SOLUTIONS

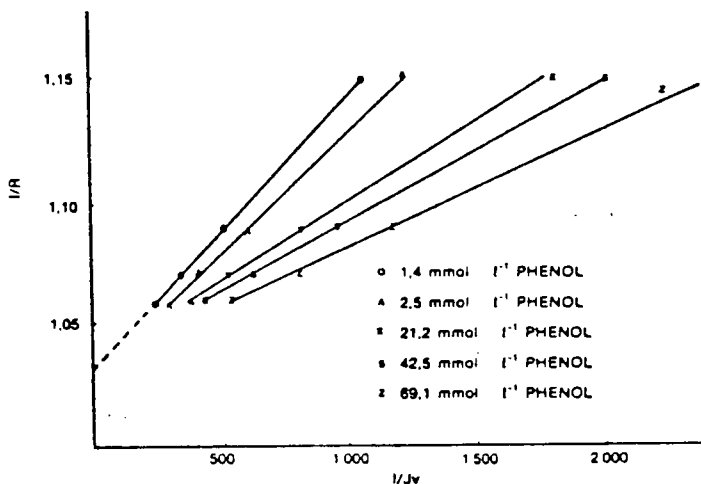


FIGURE 4: $1/J_v$ vs $1/R$, FT-30 MEMBRANE, PHENOL

Solvent (water) flux

Pure water flux and solvent (water) flux from solutions is related directly and linearly to the effective pressure and can be described by

$$J_v = L_p (\Delta P - \sigma \Delta \Pi)$$

For NaCl solutions, therefore, reduction in water flux at higher concentrations can be accounted for by the higher osmotic pressure and hence lower effective pressure. Phenol solutions also exhibit a marked decline in water flux with increasing concentration. However,

this reduction cannot be accounted for by higher osmotic pressures in the feed solution since the osmotic pressure of a 50 mmol/l solution is only about 140 kPa (20 psi) while a flux reduction of more than 50% was found for this feed concentration compared to very dilute solutions. This effect is very pronounced for the FT-30 membrane and is shown in Figure 5 where J_v is plotted against operating pressure for different solutions.

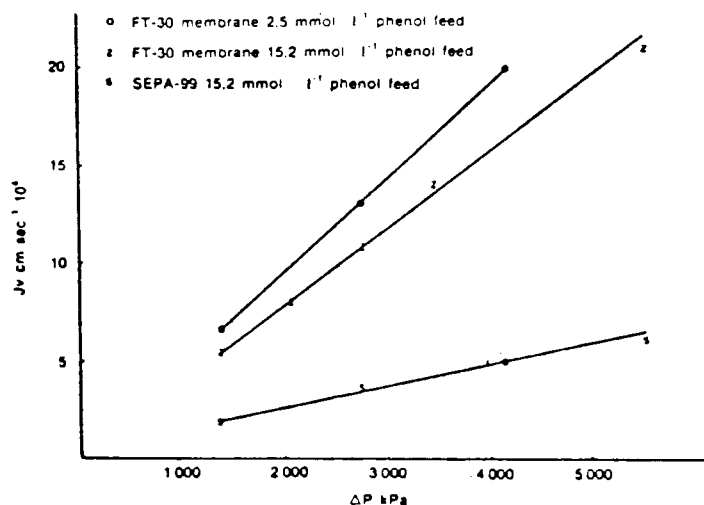


FIGURE 5: WATER FLUX (J_v) vs OPERATING PRESSURE (ΔP): PHENOL FEED SOLUTIONS

There are two possible explanations for the increase in hydraulic resistance at higher concentrations. Firstly, the osmotic conditions right at the membrane surface or just inside the membrane skin may be completely different from the osmotic pressure in the bulk solution. As a result the true $\Delta\pi$ may be much higher than $\Delta\pi$ measured in the bulk solutions and the effective pressure driving force may be much lower than measured. It should be pointed out, however, that concentration polarization occurred only to a very limited extent under the flow conditions that prevailed in the test cells and that the apparent osmotic pressures from plots of J_v vs ΔP are close to zero even for relatively high concentrations (2 000 mg/l).

A second possible explanation is that phenol may be sorbed by the membrane material either on the membrane surface, or more likely, in the very finely porous structure of the membrane, thereby increasing the flow resistance of the membrane. If sorption takes place, then obviously osmotic pressures will be very low and will not affect flux rates. In order, therefore, to obtain some information on the sorption of phenol by different membranes a series of sorption and desorption tests was done.

Phenol sorption and desorption

These tests were done using the two procedures described above, i.e. sorption by rolled strips of membrane in test tubes, and sorption and desorption from pieces of membranes in a diffusion cell.

Data obtained in one series of tests using strips of rolled membrane in test tubes are summarized in Table 3 which shows the amounts of phenol sorbed by the different membranes from solutions of different concentrations. This table shows that the bulk of phenol sorbed by the FT 30 membrane can be ascribed to sorption by the polysulphone. However, the amount sorbed per unit mass is much higher for the polyamide than for either the polysulphone or the cellulose acetate.

It was not possible to accurately determine the mass of aromatic polyamide and polysulphone per unit area in the FT 30 membrane because of irregularities in the thickness of the membrane and because of the extremely small amount of polyamide in the skin. The average

mass of polyamide and polysulphone per unit area of FT 30 membrane determined from a number of samples of different sizes as well as the average mass of cellulose acetate (including skin and porous structure) are as follows :

Aromatic polyamide = $0,02 \text{ mg cm}^{-2}$
 Polysulphone = $1,88 \text{ mg cm}^{-2}$
 Cellulose acetate = $2,4 \text{ mg cm}^{-2}$

In addition to the above procedure of obtaining data by difference, the tests in the diffusion cell gave some independent measurements. The change in phenol concentration in the solutions on either side of the membrane was monitored in order to differentiate between sorption (and desorption) by the polyamide and polysulphone sides of the membrane. (Control tests showed no sorption by the polyester backing material).

TABLE 3: SORPTION DATA FOR FT-30, POLYSULPHONE AND SEPA-99 MEMBRANES AND PHENOL SOLUTIONS

Membrane	mmol / 25 ml, T_0	mmol / 25 ml at T_0 + 2 hrs	mmol / 25 ml at T_0 + 5 hrs	mmol / 25 ml at T_0 + 24 hrs	mmol phenol sorbed	mmol phenol sorbed per g of membrane material
FT-30	0.025	0.0083	0.0050	0.0028	0.0222	0.12
PS	0.025	0.0032	0.0050	0.0037	0.0213	0.03
CA	0.025	0.0123	0.0097	0.0089	0.0161	0.02
FT-30	0.05	0.0216	0.0148	0.0068	0.0284	0.89
PS	0.05	0.0226	0.0171	0.0151	0.0349	0.05
CA	0.05	NA	NA	NA	NA	NA
FT-30	0.1	0.0620	0.0461	0.0226	0.0774	0.935
PS	0.1	0.0702	0.0528	0.0294	0.0706	0.10
CA	0.1	0.0741	0.0442	0.0357	0.0643	0.07
FT-30	0.175	NA	0.0727	0.0491	0.1259	1.09
PS	0.175	NA	0.0798	0.0570	0.118	0.17
CA	0.175	NA	NA	NA	NA	NA
FT-30	0.25	NA	NA	0.0829	0.1671	1.39
PS	0.25	NA	NA	0.0930	0.1570	0.23
CA	0.25	NA	NA	0.1047	0.1453	0.17

*Amount phenol adsorbed by aromatic polyamide was determined from the difference between the amount adsorbed by the FT-30 membrane and the polysulphone membrane and this difference was divided by the amount of polyamide in the strip of membrane

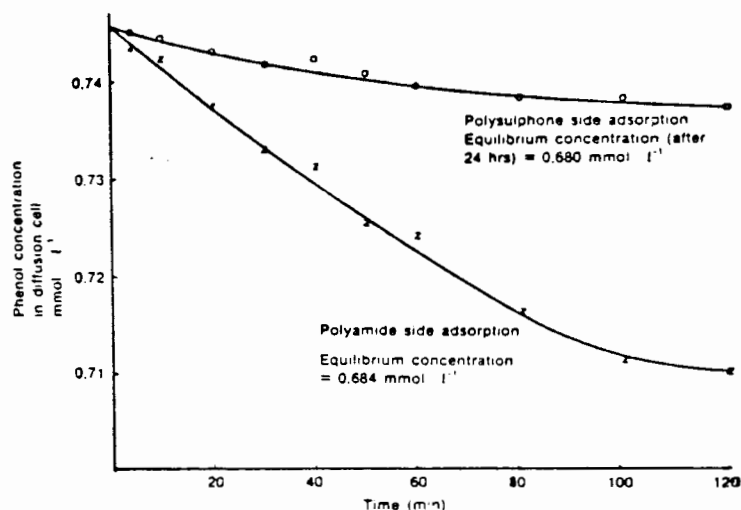


FIGURE 6. SORPTION FROM $0.745 \text{ mmol l}^{-1}$ PHENOL SOLUTION BY THE POLYAMIDE AND POLYSULPHONE SIDES OF FT-30 MEMBRANE

Figure 6 shows the change in concentration of a $0,745 \text{ mmol l}^{-1}$ phenol solution in the two chambers of the diffusion cell separated by the FT-30 membrane. It shows that sorption by the polyamide skin proceeds more rapidly than by the polysulphone side but that the equilibrium concentrations are about the same.

The same phenomenon is also observed in desorption tests. Figure 7 shows the increase in phenol concentration in the solutions in the diffusion cell compartments as a result of desorption from a FT-30 membrane equilibrated in a 130 mmol l^{-1} phenol solution. After removal from the phenol solution after 24 hours the membrane was instantly rinsed in distilled water, and then placed in the diffusion cell and both chambers of the cell filled with distilled water and the changes in concentration monitored. Desorption proceeds much faster from the polyamide side than from the polysulphone side. These observations seem to be contradictory since faster sorption by the polyamide indicates stronger forces of attraction while faster desorption indicates weaker forces of attraction.

Similar results were found for the cellulose acetate membrane. Sorption and desorption in this case too occurred much faster from the skin side than from the porous understructure of the membrane. The faster rates of both sorption and desorption from the skin sides of the membranes may be explained by the fact that sorption possibly takes place in the very finely porous membrane structure rather than on the membrane surface. This means that the denser skin will sorb more phenol per unit membrane area than the porous understructure giving a higher concentration gradient driving force from the skin side when the membrane is placed in pure water and therefore a faster rate of desorption. The same explanation also holds when the membrane is placed in a phenol solution where the driving force for sorption is larger on the dense skin side than at the more porous understructure side.

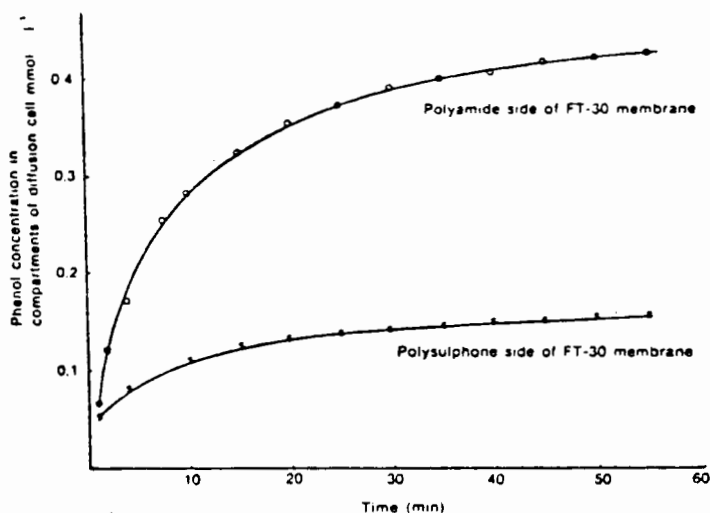


FIGURE 7: DESORPTION FROM A FT-30 MEMBRANE EQUILIBRATED IN 130 mmol l^{-1} PHENOL

Phenol permeation and diffusion

According to the solution-diffusion and other membrane transport models solute transport through dense reverse osmosis membranes takes place by a diffusion mechanism under the driving force of the chemical potential gradient. In order to obtain data on permeation and diffusion rates of phenol through the different membranes a series of tests was conducted using the diffusion cell.

Prewashed FT-30, polysulphone and SEPA 99 membranes were used in these tests in which concentrated phenol solutions were put in the skin side compartment of the diffusion cell and pure water in the other cell. The rate of change of phenol concentration in the clean water cell was then monitored until a constant rate was established. Figure 8 shows the rate of

phenol permeation through the three membranes. The phenol solution on the skin side of the membranes had a concentration of 130 mmol l^{-1} for all three the membranes.

The rates of permeation through the 7.07 cm^2 exposed membrane area as calculated from the linear slopes of the plots in figure 8 are

FT-30	:	$7.3 \times 10^{-7} \text{ mmol cm}^{-2} \text{ sec}^{-1}$
Polysulphone	:	$17 \times 10^{-7} \text{ mmol cm}^{-2} \text{ sec}^{-1}$
SEPA 99	:	$37 \times 10^{-7} \text{ mmol cm}^{-2} \text{ sec}^{-1}$

The very low permeation rate through the FT-30 membrane compared to the cellulose acetate SEPA-99 membrane is in line with phenol reverse osmosis data on these two membranes. However, the fact that the permeation rate through the polysulphone membrane is also lower than through the cellulose acetate membrane is unexpected in view of the more porous nature of the polysulphone membrane. This fact indicates that diffusive solute transport (at zero volume flux) depends to a greater extent on solute-membrane interaction and less on porous structure.

From these data it may be inferred that phenol interacts more strongly with aromatic polyamide than with either polysulphone or cellulose acetate, resulting in higher phenol sorption by the polyamide, stronger forces of attraction and lower rates of diffusion.

Sourirajan and Matsuura (1977) explain the high rate of phenol permeation through cellulose acetate membranes by the preferential sorption of phenol (to water) at the solution-membrane interface and the "mobility" of phenol in the vicinity of the membrane pores.

A comparison of the sorption and desorption and permeation data on the cellulose acetate and polysulphone membranes indicates that the amount of phenol sorbed by polysulphone is higher than that sorbed by the cellulose acetate per unit membrane area and per unit membrane mass and that the rate of desorption from cellulose acetate is much higher than from polysulphone under similar conditions (data not included in this paper). These data point to relatively strong forces of attraction between polysulphone and phenol compared to cellulose acetate which may explain the higher rates of phenol permeation through the cellulose acetate membrane.

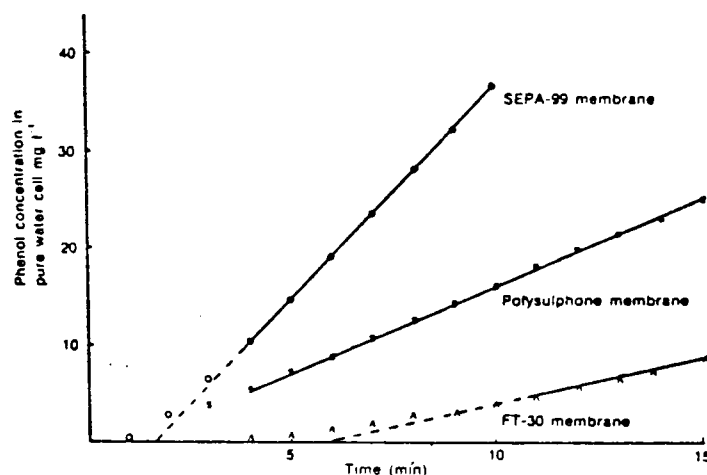


FIGURE 8: PHENOL PERMEATION vs TIME AT $J_v = 0$

The rate of permeation through the polyamide skin of the FT-30 membrane was determined both directly and computed from the following :

$$\frac{1}{J_{SP} \text{ FT 30}} = \frac{1}{J_{SP} \text{ polyamide}} + \frac{1}{J_{SP} \text{ polysulphone}}$$

using J_{sp} values for the FT-30 membrane and polysulphone membranes from Figure 8.
 J_{sp} polyamide skin = 12.8×10^{-7} mmol \cdot cm $^{-2}$ sec $^{-1}$

Measured permeation values ranged between 20 and 50×10^{-7} mmol \cdot cm $^{-2}$ sec $^{-1}$.

These data together with data on the hydraulic permeability of the membranes indicate that resistance to hydraulic flow is determined by the skin of the membrane while resistance to diffusion is mainly caused by the relatively thick porous understructure.

The values given above are for the phenomenological process of permeation which does not necessarily represent diffusion in the membrane. In order to determine diffusion rates the actual concentration of solute in both surface layers of the membrane must be known. These values are not readily obtainable especially in laminated membranes such as the FT-30 membrane, but also in asymmetric membranes which can be considered as a very dense membrane on a porous support of the same material.

CONCLUSIONS

The following conclusions can be drawn :

- (i) Phenol and higher homologues are effectively rejected by the FT-30 membrane (>90%) while the SEPA 99 cellulose acetate membrane has virtually no phenol rejection.
- (ii) Water flux through the FT-30 and to a lesser extent through the cellulose acetate membrane shows a significant drop with increasing phenol concentration in the feed solution which cannot be accounted for by higher osmotic pressures of the feed solution. Two possible explanations for this phenomenon are that the osmotic pressure at the membrane surface may be much higher than in the bulk solution, or secondly that phenol is sorbed in the very finely porous structure of the membrane and that this causes an increase in the resistance to diffusion of water through the membrane.
- (iii) Phenol rejection by the FT-30 membrane follows the classical pattern of increasing rejection at higher pressures, while rejection by the SEPA 99 membrane decreases as the pressure is increased.
- (iv) The rates of phenol sorption and desorption from the skin sides of the membranes are higher than from the support sides of the membranes indicating larger sorption and-desorption driving forces at the skin sides. A possible explanation is that sorption takes place in the porous structure of the membrane rather than on the membrane surface and that the sorption capacity is much higher in the very finely porous skin structure than in the coarsely porous support giving the higher driving forces.
- (v) The poor rejection of phenol by the cellulose acetate SEPA 99 membrane is a result of positive phenol sorption by the cellulose acetate and the relatively high rate of diffusion in the membrane.

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- (i) Dr Robert Petersen of Filmtec Corp. for making the reverse osmosis test unit and membrane samples available for this project and for his assistance and advice.
- (ii) Ionics Inc for making SEPA-99 test samples available.
- (iii) The Water Research Commission for financial support to C F Schutte.

NOMENCLATURE

C_0 , C_{fw} , C_p solute concentration in feed, at membrane surface and in permeate, mmol l^{-1} .
 J_v total volume flux, mmol \cdot cm $^{-2}$.sec $^{-1}$
 J_w pure water flux, cm 3 .sec $^{-1}$

J_s	solute flux, $\text{mmol} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$
J_{sp}	solute permeation rate (at $J_v = 0$) $\text{mmol} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$
L_p, L_{pd}, L_p	phenomenological coefficients of the linear laws as applied in Kedem-Katchalsky model.
L_p	hydraulic coefficient, $\text{cm} \cdot \text{sec}^{-1} \cdot \text{kPa}^{-1}$
ΔP	operating pressure, kPa
R	membrane rejection coefficient
R_x	asymptotic maximum rejection
$\Delta \Pi$	osmotic pressure difference, kPa
σ	reflection coefficient in Kedem-Kachalsky model
ω	solute permeability coefficient in Kedem-Katchalsky model.

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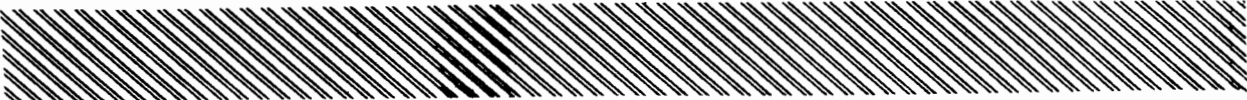
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Prospects for the Use of Reclaimed Water for Drinking Water Purposes

M.R. Henzen * and

C.F. Schutte **



ABSTRACT

The prospects for the direct use, for drinking water purposes, of water reclaimed from sewage effluents are considered. It is pointed out that a potential for direct reuse exists where projected demands for fresh water focusses on the importance of providing public health reassurances and on the strategy being followed in South Africa and SWA/Namibia to provide the necessary reassurances.

It is concluded that the prospects for the use of reclaimed water for drinking purposes are very promising, firstly because the supply-demand situation in South Africa is in a very delicate position and secondly because health and other authorities have developed a very sound control strategy to protect public health.

1. INTRODUCTION

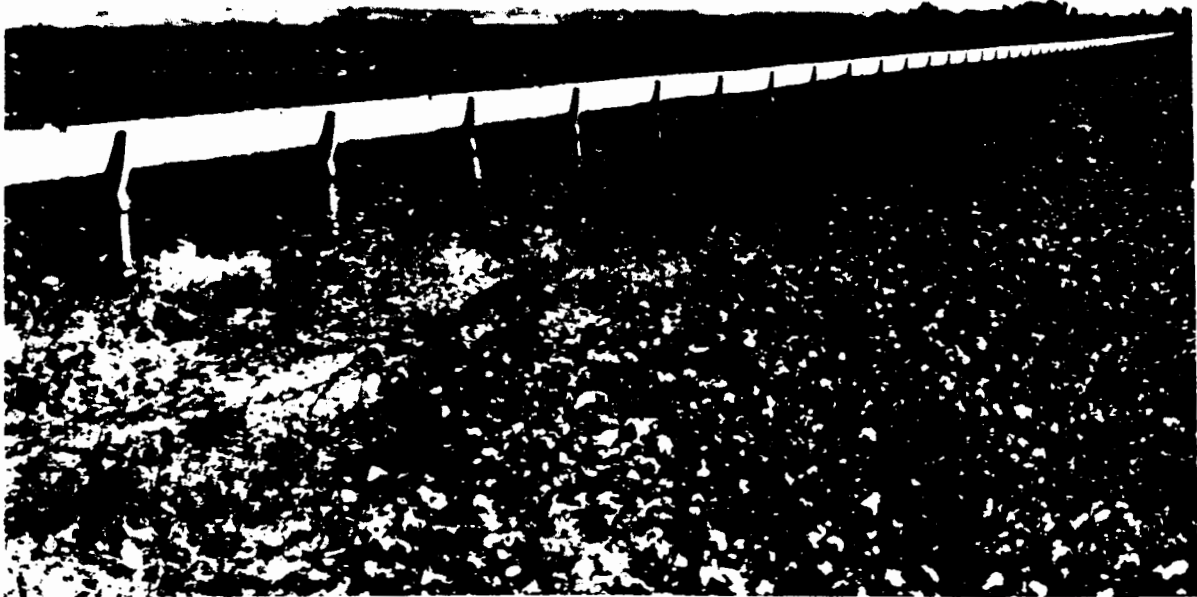
Demands on fresh water supplies are escalating worldwide as a result of population growth, improved standards of living, economic and industrial growth and increased

* Chairman ** Project Adviser
Water Research Commission, Pretoria
South Africa

agricultural activities. In many areas economically available fresh water resources are being exploited to their maximum assured yields. South Africa, being a water-short country like Israel, is in the position that the assured yield of fresh water resources will be exceeded by demand on a national basis shortly after the turn of the century (1). In fact, to sustain economic and industrial growth the supply to certain areas has already had to be augmented by inter-basin transfers of water (2).

Research efforts on measures to augment and effect optimal utilization of existing water supplies have been intensified since the Water Research Commission was established in 1971. Research is being concentrated on aspects such as wastewater purification and reclamation technology, optimization of dry cooling, optimization of irrigation practices and desalination (3).

Water quality is another relevant aspect when considering the water supply and demand situation. A steady deterioration in the quality of many water resources has been experienced concurrently with the increasing demands on these resources. Deterioration in quality is caused mainly by increasing return flows from municipal and industrial wastewater treatment facilities and run-off from urban, agricultural and mining areas. In addition, the multitude of chemicals,



some of "uncertain character" which are continuously being developed and produced and which often find their way to water courses and water bodies is a matter of grave concern.

Many fresh water surface resources receive large proportions of purified effluents - up to one hundred percent during periods of low flow. Purification is, however, in most cases still being done by the conventional processes such as clarification, filtration and disinfection, with inherent limitations for treating polluted surface waters. The health implications of this situation are causing concern internationally and in some instances resort has already **been** taken to advanced processes such as activated carbon adsorption.

In South Africa the water supply situation could become critical within the next decade and, therefore, measures to overcome this problem are currently being developed. Water reclamation and reuse has been identified as the one measure which could significantly contribute to solving this problem. Some considerable effort is being devoted to the technological development of reclamation with water derived from polluted resources.

In addressing the question - "What are the prospects for the use of reclaimed water for drinking purposes?" - it should be evident that any answer can only apply to a given set of circumstances relevant to a particular locality, district or country. In general, however, it can be said that where projected demands for fresh water exceed currently economically available supplies, a potential for the use of reclaimed water for drinking purposes exists and reuse could play a most important role as an alternative to making costly conventional supplies.

In our opinion the prospects for the use of reclaimed water for drinking purposes are very promising, not only as a result of the narrowing gap between water supply and demand and the deteriorating quality of existing conventional supplies, but also because a firm basis of knowledge already exists on water reclamation technology, its economical application and associated health considerations. In this regard, we have pleasure in announcing the publication of a "Guide for the planning design and operation of water reclamation plants" compiled in South Africa under the auspices of the Water Research Commission by a firm of consulting engineers on the basis of the experience gained over a decade with water reclamation in South Africa. The

Guide is intended to assist local authorities and industries in planning for water reclamation and reuse and to serve as a design guide for engineers involved in the field of water treatment and reclamation.

Notwithstanding the aforementioned, it is recognized that a number of aspects, viz. public acceptance and economical considerations still require further attention before unrestricted reuse of reclaimed water will become a widely accepted practice. In South Africa these latter aspects are currently receiving serious attention.

To motivate our statement that the prospects for the use of reclaimed water for drinking purposes are most promising, the following are dealt with in this paper: current practice of and expected future trends in the use of reclaimed water; the potential for reclamation; public health considerations and public acceptance. In view of the controversy regarding the possible health effects of organics at very low concentrations in drinking water and its influence on the prospects for reuse, the accent of this paper is placed on the importance of providing the necessary public health reassurances where the use of reclaimed water is contemplated, and on the strategy being followed in South Africa to provide these reassurances.

2. REUSE OF WATER RECLAIMED FROM WASTEWATER

There are a number of ways in which purified wastewater is being reused for drinking water purposes. The different forms of reuse are briefly outlined.

Unplanned, unintentional or covert reuse occurs when purified sewage effluent is discharged to a water body from which it is subsequently abstracted in dilute form and then purified in a conventional water purification plant. This uncontrolled indirect form of reuse has been practised worldwide to a greater or lesser extent and will certainly still remain for many years to come. In this form of reuse the self-purification and dissipation capacity of the water body is relied upon as a safety barrier for the protection of the water quality. Limitations in this regard have recently become apparent as a result of the application of newly developed highly sensitive analytical techniques which revealed the presence of a large number of organic compounds in drinking water supplies (4).

Planned indirect reuse involves the knowledgeable discharge of tertiary treated effluents upstream of a water supply intake. This form of reuse presents a much more acceptable alternative to that mentioned above, since meaningful control can be exerted over discharges to the water body by way of efficient wastewater purification backed up by a supplementary effluent quality surveillance programme.

Groundwater recharge involves the injection or percolation of tertiary treated effluents into aquifers supplying potable water. Only reclaimed water of the highest quality should be used for recharging, to ensure that irreversible pollution of such resources of drinking water does not take place.

Reclamation for direct potable reuse or the "pipe to pipe" concept, involves the purification of wastewater to potable standards and its integration with conventionally purified surface and groundwaters for direct distribution for domestic use. Since the safety barriers of self-purification, dissipation and retention do not exist in this form of reuse, alternatives have had to be established. In Southern Africa potable water quality and public health is being ensured for potable reuse schemes by following a total reclamation strategy, i.e. one which includes the following lines of defence:

- Segregation of domestic and industrial effluents, supplemented by sewage "catchment" quality control;
- the application of effective and reliable reclamation processes with at least two safety barriers for each group of contaminants; and
- intensive monitoring and surveillance of reclamation processes and the quality of the product water.

The prospects for reclamation for direct potable reuse will be considered in more detail further on.

3. THE POTENTIAL FOR RECLAMATION FOR POTABLE PURPOSES

In considering ways and means of meeting projected demands, the economics of reclamation as a short-term alternative to making conventional supplies available, as well as serving as a long-term supplementary and stand-by resource should be evaluated.

The harnessing of surface fresh water resources is usually highly capital intensive, but involves low operating cost. The distance of fresh water impoundments from the user can also constitute a considerable cost factor. In contrast, reclamation requires relatively low capital investment, but production costs are high. The water is produced virtually at the point of use and an assured fresh water supply is available. Reclamation, therefore, presents an alternative of making water available in the short-term, thereby creating an opportunity to postpone big capital investment for a period of time in instances where this may be desirable. Reclamation facilities could, in such instances be regarded as assured fresh water supplies in the shorter term. When the big capital intensive impoundments or water transfer schemes are then later constructed, the reclamation plants can serve as supplementary sources as required or can be used to produce water for specific requirements.

In assessing the potential for reuse and other alternatives to augment supplies, the two options, viz. purification and indirect reuse as opposed to reclamation and direct reuse should be evaluated. A major factor to be considered is the economics of the two alternatives to produce the same quality of final water. In this regard, it should be noted that whereas the reclamation and purification costs can be readily determined, the hidden costs in the indirect system are more difficult to assess accurately.

Turning now to South Africa as a specific case in point, the potential for reuse is the result of a number of unfavourable climatic factors: The country lies in the drought belt of the Southern Hemisphere and has a mean annual precipitation of only 483 mm compared to 736 mm for the USA, and to a world average of 860 mm (5). Furthermore, there is poor distribution of rainfall and consequently, non-uniform distribution of run-off. Other contributing factors are the strong seasonal character of rainfall; increasing variability with decrease in rainfall; high average temperatures, low relative humidity and thus high evaporation rates.

It should also be pointed out that the potential for in-plant reuse in industry, especially the major industries in South Africa is already being exploited to a large extent, for example at SASOL (oil from coal industry), water is being reused to the ex-

tent that there is virtually no effluent from the plant. Similarly, in the steel, power generation, pulp and paper and chemical industries reuse is being practised as far as possible.

The potential in Southern Africa for use of water reclaimed for drinking water purposes does not only exist, but is in fact already being relied on as an assured supply in the case of Windhoek (SWA/Namibia). Further positive steps in South Africa are: the taking over of the 4,5 Ml/d experimental Stander Water Reclamation Plant in Pretoria by the local authority on a temporary basis to demonstrate the feasibility of reclamation for, and under the specific constraints of, the City of Pretoria (the reclaimed water is not being distributed for potable purposes); the construction of a 4,5 Ml/d demonstration plant in Cape Town; and a local authority on the West Coast is at present in the planning stage of establishing a reclamation scheme.

4. PUBLIC HEALTH CONSIDERATIONS

Since public health considerations play a key role as far as the prospects for direct reuse are concerned this aspect will be considered in greater detail. In any potential direct reuse situation, the health authorities will have to be convinced that reclaimed water will in no way be harmful to public health. Their support is considered essential before reclamation of water for potable use can be practically implemented. Producing the necessary health guarantees is a most difficult task. The conventional approach of establishing a list of standards and monitoring the water quality to assure compliance with these standards is not feasible in the case of reclaimed water because this water originates from sewage which could contain literally hundreds of compounds, many in very low concentrations. Thus another approach is required.

The approach adopted in Southern Africa referred to as a total reclamation strategy, combines three integrated lines of defence. This strategy, which is currently receiving much attention in South Africa in the form of extensive research and development studies by various multi-disciplinary teams of research scientists and engineers, guided and coordinated by representatives of government, health and local authorities, will be dealt with in-depth in this section.

4.1 First line of defence: Sewage "catchment" quality control

Where reclamation of wastewater for potable reuse is considered, the starting point in the process of safeguarding public health is to control the type of wastewater which is accepted for discharge in the sewage collection system. A sound first line of defence would, therefore, be to divert all industrial discharges containing potentially harmful chemicals from the domestic sewage collection system. Such a system of segregation can usually be implemented in cities with more than one sewage works and more than one outfall sewer. This is, in fact, the strategy which was followed both for the production reclamation plant in Windhoek and the demonstration reclamation plant in Cape Town.

It is not always possible to segregate all industrial effluents from domestic sewage, since in many instances, light industrial concerns, such as dry-cleaning depots, photographic shops and garages are located in predominantly residential areas, and, therefore, can only discharge to the domestic sewer. In such instances sewage "catchment" quality control, i.e. a system similar to that of catchment quality control being practised by the Thames Water Authority for the Lea River in England(6), where controlled indirect reuse is being practised, should be implemented. Such a quality control programme is currently being developed and progressively implemented for the sewage collection system serving the Pretoria sewage treatment works, which in turn, produces the effluent which is reclaimed in the Stander Water Reclamation works.

The sewage "catchment" quality control programme for Pretoria is being implemented in three phases:



- The first phase comprises a survey of every industrial and business concern served by the Pretoria outfall sewer. It will establish which chemicals are being discharged and in what quantities. This survey involves a desk study of all available information regarding sewage discharges followed by visits to each concern at which undesirable chemicals, i.e. those known to be toxic, non-biodegradable and of uncertain character, are used or produced and can thus potentially be discharged to the sewer.
- The second phase comprises an assessment of the data obtained in the first phase. Mass balances of every undesirable chemical are determined taking into account such factors as total mass and sewage flows so as to arrive at an average concentration at which such a chemical could be present over any specific period of time.
- The third phase is a practical monitoring programme for the verification of mass balances and the determination of the concentrations of specific chemicals in the raw sewage, treated wastewater and reclaimed wastewater. Based on this information an upper tolerable concentration of the chemicals in the sewage and thus also for the total mass of every chemical that can be discharged, is established.

Should practical reuse for potable purposes of the reclaimed water from the Stander plant be considered in future, further phases will have to be implemented such as providing for alternative means of disposal of chemicals or effluents identified in the previous phases and which could persist in the reclaimed water at concentrations considered to be unacceptable.

The present programme is conducted under the direct control of the responsible city health authorities with the guidance of state health authorities. The legislative means necessary to obtain all the required information is provided for in the S A Health Act of 1977.

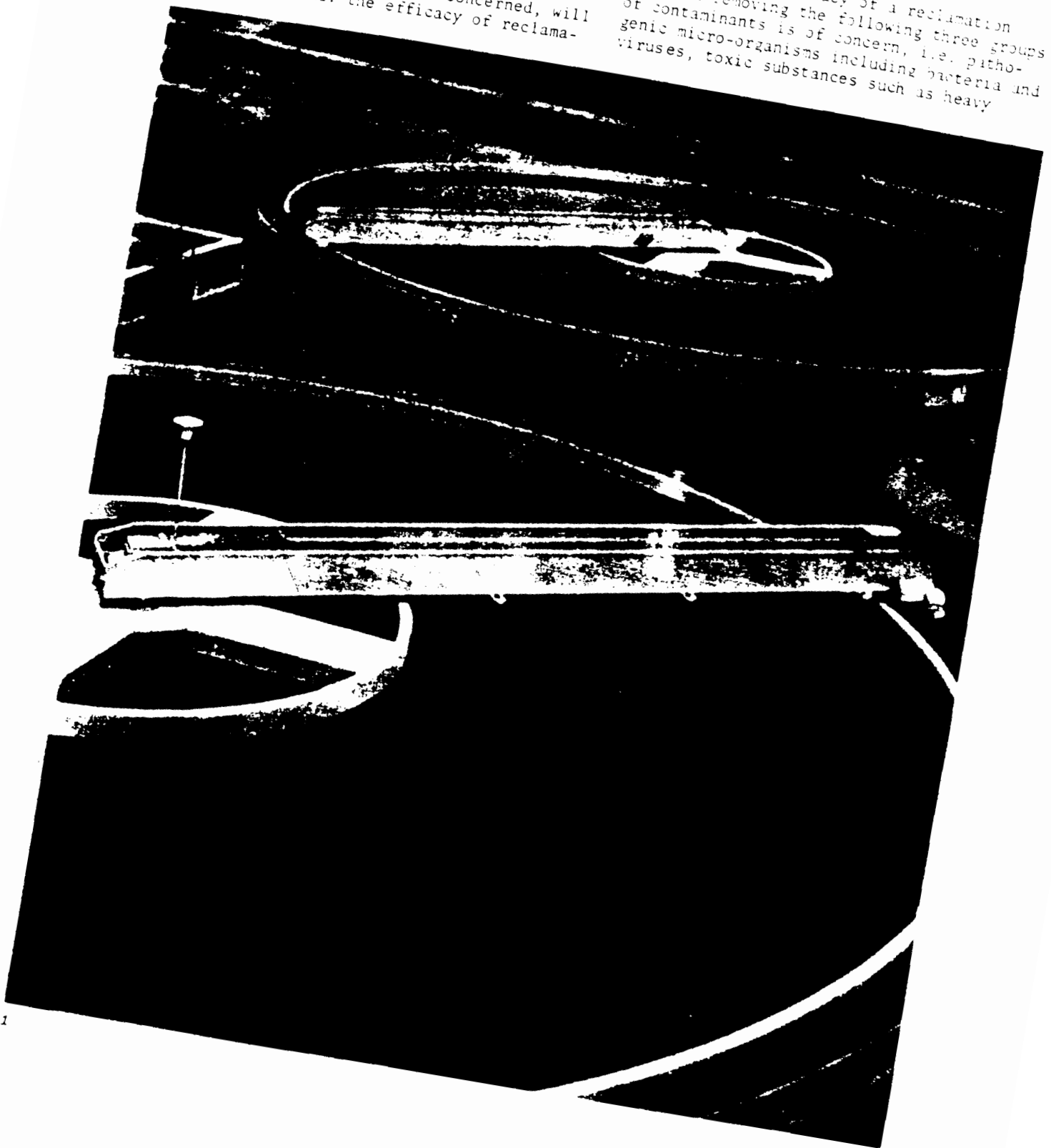
4.2 Second line of Defence: Reclamation Technology

A second line of defence proposed for a total reclamation strategy for ensuring public health is the application of efficient

reclamation technology backed by vigilant control. The technology developed for reclamation has been dealt with extensively in the literature and will not be considered here (7). However, two crucial questions dealing with safeguard to public health, as far as this technology is concerned, will be discussed, viz. the efficacy of reclama-

tion processes to remove pollutants and the reliability of these processes.

Efficacy: The efficacy of a reclamation plant in removing the following three groups of contaminants is of concern, i.e. pathogenic micro-organisms including bacteria and viruses, toxic substances such as heavy



metals and biocides, and organic chemicals which could have mutagenic terratogenic or similar effects when consumed at very low concentrations over long periods of time.

The efficacy of disinfection processes to eliminate pathogenic bacteria and viruses from reclaimed water, as well as the efficacy of processes to remove heavy metals and biocides, is well established and will not be pursued here. However, the removal of the organic chemicals suspected of having carcinogenic and other effects at very low concentrations, presently constitutes the biggest concern over drinking water supplies in general and thus even more so to reclaimed water.

A considerable fraction of the research effort conducted on water reclamation in South Africa has been directed to the objective of establishing whether existing reclamation unit processes efficiently and adequately remove organics from the treated wastewater. Results indicate that the number and concentration range of organics present in reclaimed water are substantially lower than in present-day drinking water (8,9). This work is continuing in order to obtain more confirmatory data and also to demonstrate to the health authorities that the high quality of reclaimed water can be consistently maintained in an efficiently operated water reclamation plant.

Reliability: The reliability of water reclamation plants to consistently produce water of acceptable quality is often questioned. In arguing this question, it should be pointed out that a water reclamation plant is not synonymous with an advanced wastewater treatment plant (AWT), although the same processes could be and usually are employed in both. The control and operation of a reclamation plant should encompass an additional dimension of vigilance which is usually lacking in an AWT plant.

To ensure the reliability referred to above, the following aspects require careful consideration and implementation:

- Reclamation plants should be operator-oriented to ensure maximum control of the process through continued observation, monitoring and analysis. This may seem in contrast to the modern trend of full automation and the operator playing a minor role by attending to the alarms of the automatic control and alarm systems. The accent should be on the operator to

control the plant with the aid of automated operational and control instruments.

- With respect to the training and qualifications of reclamation plant operators, it should be pointed out that high level of training is essential in developing the skills of the operating personnel. Operators should judiciously be selected not only for their intellectual and practical skills, but also for their integrity, dedication, motivation and enthusiasm. These characteristics play a key role to reliable plant operation.
- It is considered essential that reclamation plant operators acquire professional certification under an ethical code since they are intimately concerned with the health of the public.
- It is necessary to have a well-designed and implemented preventative maintenance programme for every specific plant and for every part of the different mechanical, electrical and electronics systems, supplemented by an alarm system should a failure occur.

Where the above four points have been implemented, as for example, at the Windhoek and Stander Water Reclamation Plants, the plant operation was consistently reliable and reclaimed effluents produced at these plants at all times met the stringent health and other standards set for this water.

4.3 Third line of defence: Surveillance and monitoring

The last line of defence in a total reclamation strategy is the vigilant monitoring of plant performance and surveillance of product quality, supplemented by epidemiological surveys and studies to provide the necessary public health assurances to the health authorities concerned.

- Chemical and Microbiological Surveillance
An extensive chemical and microbiological surveillance programme is currently being carried out on reclaimed water from the Stander Water Reclamation Plant and also, to serve as a comparison, on some of the major conventional drinking water supplies of South Africa. The surveillance programme includes six microbiological parameters including enteric viruses; the conventional chemical parameters and a

host of organic micro-pollutants, organo-halogens, as well as a number of organic pollution indices.

Results to date confirm that as far as these parameters are concerned the reclaimed water compares very favourably to and is indeed superior in quality to many of the conventional supplies, especially in as far as the "sensitive compounds" such as volatile organohalogens and other organic micropollutants are concerned.

- Biological Monitoring and Assaying

The monitoring of the behaviour of living organisms in reclaimed water serves as a wide range indicator of the quality of the reclaimed water, both in the short- and long-term. In addition, this type of monitoring provides considerable psychological reassurances as to the safety of the drinking water, a factor considered of prime importance.

Bio-monitoring involves the continuous observation and recording of one or more organism responses, e.g. fish gill-operculation rate or rate of oxygen consumption, and transmission of these responses by a system which allows "real time" warning of detrimental changes in water quality. It follows that bio-monitoring requires relatively sophisticated instrumentation and is inherently sensitive having a rapid response rate.

Bio-assaying involves the analysis and comparison of physical parameters such as whole organism well-being, growth rates, reproduction, feeding patterns, together with limited routine histopathological examination and bio-accumulation studies. It follows that bio-assaying measures "longer" term effects and hence cannot, in the same sense as bio-monitoring systems, be used as a "real time" alarm system. Certain variations can, however, be applied to act as an alarm system for acute situations.

Bio-assays can be conducted in many different ways and can range from tests involving bacteria such as the Ames test, tissue cultures and assays involving fish and bivalves. All of these can play a role in the assaying of reclaimed water quality. Different biomonitoring and assaying techniques are currently being evaluated for application in water reclamation schemes.

- Epidemiological Surveys and Studies

In view of the need for reassurance that the ingestion of reclaimed water will not have any untoward long-term health effects, it is considered essential that extensive epidemiological surveys be carried out over the long-term where direct reuse is practised.

With the abovementioned objective in mind, an epidemiological survey programme was launched in 1973 in the City of Windhoek to confirm the authoritative opinion that no harmful effect on public health would result from the consumption of reclaimed water.

Data collected to date have not shown any noticeable or meaningful increases in the incidence of infection during periods when the Windhoek population consumed water augmented by reclaimed water as compared to the incidence during times when only conventional water sources were used (10). It should, however, be noted that from the outset of the project, it was clear that it would not be possible to draw meaningful conclusions for several years in the case of waterborne infectious diseases and for a decade or more in the case of chronic noncommunicable diseases.

An opportunity to develop and initiate epidemiological studies well in advance of the actual implementation of reuse presented itself in the City of Cape Town where a demonstration water reclamation plant is at present being constructed. It is envisaged that the reclaimed water produced by this facility will be integrated into the conventional water supply of the City in the near future. An epidemiological programme is at present being developed and will be introduced in 1980. The proposed studies will include a statistical comparison of the occurrence of human disease with water supply and an epidemiological study of the health patterns of the community as a whole, including that area which will receive reclaimed water from the demonstration plant. This will comprise both a comparison of this community before and after the introduction of direct reuse, as well as comparison with other communities receiving water supplies entirely from conventional sources. The parameters to be studied will have relevance to physical, socio-economic, cli-

matic and topographic characteristics of the area and, more important, to the demographic morbidity and mortality status of the community to be sampled and its control.

Epidemiological studies constitute the final link in the strategy for protection of public health where reclaimed water is being distributed, since the ultimate reassurance will only be provided by results from studies such as these. One of the major problems, however, remains the great difficulty with which the effects of reclaimed water consumption are to be separated from the effects of any one or a combination of other variables on the study population. Nevertheless, every endeavour is being made to conduct this final reassurance and in this way, to pave the way for the acceptance of reclaimed water for potable purposes.

5. PUBLIC ACCEPTANCE OF REUSE

A most important facet of an overall strategy for reuse of water reclaimed from wastewater for drinking water purposes, is to secure public acceptance for such a scheme. Surveys to determine public attitudes to water reclamation and reuse have indicated that the two main reasons for the rejection of this type of reuse are psychological repugnance and doubts about health effects. Both of these prejudices can be overcome by well-planned and carefully executed public relations programmes which should be aimed at providing sufficient information to allay fears and false conceptions.

A case in point is the public acceptance of reclaimed water in Windhoek in 1969 where virtually no resistance was experienced. This was accomplished by pointing out to the public that water supplies were insufficient and that conventional resources to augment them are very expensive to harness and that development, growth and standards of living could have deteriorated if additional supplies were not provided. Furthermore, many plant demonstrations were held for the public to indicate the high degree of developed technology being applied in reclamation to produce a wholesome and acceptable drinking water. Great care was taken with the public media to ensure that this delicate and potentially emotional matter was not misconstrued, thereby awakening public resistance.

6. PROSPECTS FOR THE REUSE OF RECLAIMED WATER FOR DRINKING PURPOSES

It has been pointed out that in the field of drinking water supply, the world today has to contend with two problems of increasing magnitude, viz. the rapidly narrowing gap between water supply and demand, especially in "water short" countries, and a steady deterioration in the quality of conventional surface water resources. It was further indicated that the reuse of reclaimed water could significantly contribute towards surmounting both problems. There are however, certain aspects related to reclamation and reuse on which ongoing research is required to provide the necessary reassurances with respect to the unrestricted reuse of reclaimed water. These aspects are mainly concerned with public health and apply equally well to the use of potable water derived from polluted surface resources.

It is impossible to respond with a categorical "good" or "bad" to the question "what are the prospects for the reuse of reclaimed water for drinking water purposes?" The answer must be motivated on grounds of the current water supply position in a specific locality and also in the light of the operational and control strategy to be followed for reclamation schemes as such.

Bearing these factors in mind, it can be stated that the prospects for the reuse of reclaimed water for drinking purposes are very promising in certain areas of South Africa, firstly because the supply-demand situation is in a delicate balance and secondly because health and other authorities have developed a very sound control strategy incorporating various lines of defence to protect public health.

With the progressive release of new information on reclamation as it becomes available from various research projects and operational plants both in South Africa and the rest of the world, these prospects should greatly improve.

In conclusion then, it is our contention that in the not too distant future, reclamation for potable purposes will become a well-established practice.

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REJECTION OF ORGANICS BY REVERSE OSMOSIS: A NEW PREDICTIVE MODEL

C. Frik Schutte* and Georges Belfort**

* Water Research Commission, P. O. Box 824, Pretoria, 0001 R.S.A.

** Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180-3590 USA

Solvent and solute solubility and diffusivity in the membrane are measurable properties used to describe the influence of solute, solvent, and membrane interactions on membrane performance. Different researchers have attempted to correlate rejection coefficients with phenomenological parameters such as solubility parameters with limited success.^{1,2)} Others have used separate polar and steric parameters to correlate rejection for cellulose acetate and aromatic polyamide membranes.³⁻⁵⁾ The development of these theories are dependent on experimental data, therefore, are limited from a fundamental viewpoint, although they may be quite useful for practical applications. Another limitation is that some of these approaches are one-dimensional, in that they correlate only one parameter such as ionic, polar, steric, or non-polar character with rejection.⁶⁾

Here we report on the development and testing of a comprehensive theoretical basis for predicting a priori the preferential sorption of organic compounds into synthetic membranes from dilute solution. This comprehensive thermodynamic formalism called the solvophobic theory (ϕ) has been adapted and successfully tested for aqueous phase adsorption of aliphatic and aromatic compounds onto activated carbon.^{7,8)}

General Solvophobic Approach

The solvophobic (ϕ) theory describes the tendency of a surrounding solvent medium to influence aggregation or disassociation of those molecules with considerable microsurface areas exposed to the solvent medium. In the solvophobic treatment, sorption is considered a reversible reaction between the sorbate molecules, S_1 , and the membrane, M, to form the adsorbed complex, S_1M at the surface of the membrane $S_1 + M \rightleftharpoons S_1M$. The effect of the solvent on this reaction is obtained by subtracting the standard free energy change for the reaction in the gas phase from that in the presence of the solvent (taking as standard states $X_k^o = 1$, $p_k^o = 1$ atmosphere ideal gas).

Quantitatively, this process is expressed as follows:

$$\Delta G_{(\text{solvent effect})}^{\text{net}} = \Delta G_{(\text{solvent})}^{\text{assoc}} - \Delta G_{(\text{gas})}^{\text{assoc}} = -RT \ln K_1 \quad (1)$$

or

$$\Delta G_{(\text{solvent effect})}^{\text{net}} = \Delta G_{j, S_1 M}^{\text{net}} - \Delta G_{j, S_1}^{\text{net}} - \Delta G_{j, M}^{\text{net}} \quad (2)$$

where j represents each type type of interaction, such as the cavity, van der Waals, and electrostatic terms plus two correction terms for polymer mixing and reduced electrostatic effects because of the presence of the solvent. $\Delta G_{(\text{solvent})}^{\text{assoc}}$ is related to the experimental equilibrium constant, $K_{(\text{solvent}, i)} = X_{S_1 M} / X_{S_1} X_M$ which itself is related to the experimental sorption, the partition coefficient $k_1 = X_{S_1 M} / X_{S_1}$. For the comprehensive ϕ -model, each of the terms in Eqn. (2) is calculated explicitly; for the simplified model, the thermodynamic microsurface area change of the reaction, ΔA , in the cavity term is assumed to be proportional to the cavity surface area, TSA, of the specific sorbate and homologous series, $\Delta A = g \text{ TSA}$. Now solute flux is given by $J_s = D_1 k_1 \frac{dc}{dx}$ where $\frac{dc}{dx}$ is the mean solute gradient across the membrane, D_1 is the solute diffusion coefficient within the membrane. We obtain $\ln K_1 = \ln J_s + \text{constant}$. Thus, in this study, $\ln J_s$ is correlated with an adjusted TSA (i.e. ATSA). As a first approximation, we have assumed that both D_1 and $\frac{dc}{dx}$ do not effect solute-solubility in the membrane and are relatively constant for the series tested.

Experimental

Composite cross-linked aromatic polyamide membranes (FT 30, Film Tec, Mn) supported on a microporous

polysulfone film were tested in four 48 mm diameter cells at 25°C. The flow rate was controlled at between 0.5 and 8 l/min at steady operating pressures from 550-6900 kPa (80-1000 psi). Operation was in the recycle mode. Small volume samples (50 ml) of feed and product were taken at regular intervals. The feed reservoir contained 100 l. The same feed concentration was used for all isomers of a homologous series.

Results

The experimental data for two homologous series are plotted as $\ln J_g$ versus ATSA according to the simplified ϕ -theory in Figs. 1 and 2, respectively. Empirical hydrodynamic factors based on the ratios of the square root of the cross-sectional area of solutes using the smallest isomer as the reference, were used. Thus, $\ln J_g = \zeta f_A (TSA) + \phi$ where ζ is a constant characteristic of the homologous series $f_A = \sqrt{A_{xs}/A_{xn}}$ is the hydrodynamic corrective factor, and ϕ is the intercept.

Conclusion

Several reports have shown that size and slope are important parameters for determining rejection of homologous series.^(10,11) As mentioned above, others have correlated simple parameters such as those of Hammett and Taft and the solubility parameters as a measure of solute interaction forces with the membrane surfaces.⁽³⁻⁵⁾ In this first attempt at using a simplified version (ATSA) of a comprehensive theory of solute, solvent, and membrane interactions, we have obtained good correlations between the logarithm of the solute flux and the adjusted surface area of the solute.

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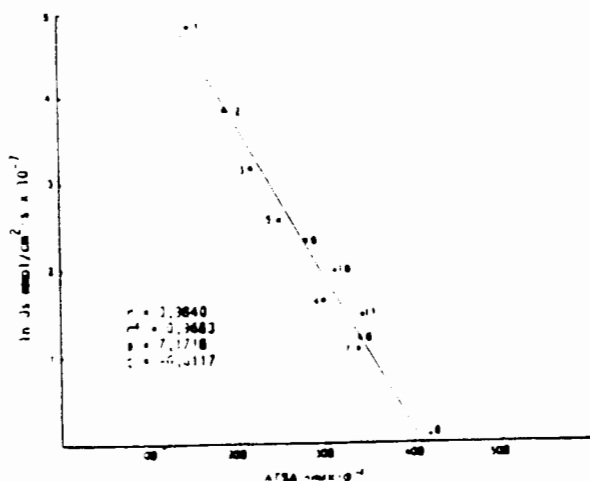


FIGURE 1. SOLUTE FLUX VS. ADJUSTED TOTAL CAVITY SURFACE AREA.
(1. Methanol, 2. Ethanol, 3. 1-Propanol, 4. 2-Propanol, 5. 1-Butanol, 6. 2-Butanol, 7. 2-Methyl-1-Propanol, 8. 2-Methyl-2-Propanol, 9. 1-Pentanol, 10. 1-Pentanol, 11. 1-Hexanol, 12. 1-Heptanol.)

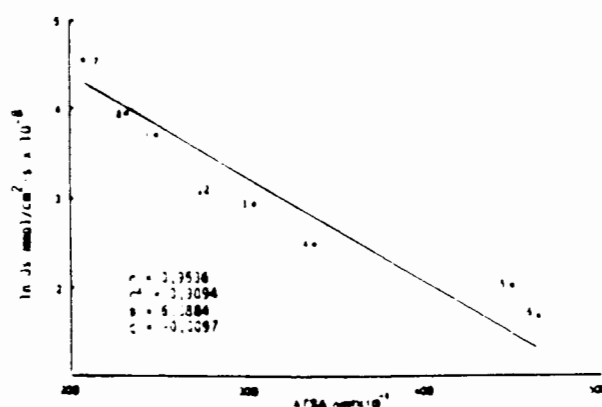


FIGURE 2. SOLUTE FLUX VS. ADJUSTED TOTAL CAVITY SURFACE AREA.
(1. Phenol, 2. 4-Methyl Phenol, 3. 4-Ethyl Phenol, 4. 4-n-Propyl Phenol, 5. 4-Isopropyl Phenol, 6. 2,6-Dimethyl Phenol, 7. Benzene, 8. Toluene.)

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