RESEARCH INTO THE TREATMENT OF EFFLUENTS WITH HIGH SALINITY AND ORGANIC CONTENTS

By Dept of Chemical Engineering, Univ of Natal

WRC Report No 123/1/87

Final Report to the WATER RESEARCH COMMISSION

for the project

RESEARCH INTO THE TREATMENT OF INDUSTRIAL EFFLUENTS WITH HIGH SALINITY AND ORGANIC CONTENTS

by the
POLLUTION RESEARCH GROUP
DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF NATAL
DURBAN

The Report is supplemented by 11 papers
emanating from the research

123/1/87

Obtainable from:

Water Research Commission
P O Box 824
PRETORIA
0001

ISBN 0 908356 71 4

SET 0 908356 73 0

ACKNOWLEDGEMENT

The research reported on in this report eminated from the following project funded by the Water Research Commission:

"Research into the treatment of industrial effluents with high salinity and organic effluents".

The Steering Committee responsible for the project consisted of

CHAIRMAN:	O O Hart	Water Research Commission
VICE CHAIRMAN:	C F Schutte	Water Research Commission
SECRETARY:	P W Weideman	Water Research Commission
MEMBERS:	T P M Young	Binnie & Partners
	J D Raal	University of Natal
	G C D Claassens	Dept Water Affairs
	Q Stubbings	SAFCI
	S Roets	S A Tanners Association
	F E Raimondo	Ass of Pulp, Paper and Board Manufacturers
	C J Davies	SAPPI
	J P Theunissen	African Products
	J S M Venter	NTRI
	D R Cooper	LIRI
ALTERNATES	J Cowan	Binnie & Partners
	F G N Neytzell-de Wilde	University of Natal
	H J Best	Dept Water Affairs
	A Hammond-Tooke	SAFCI
	G Lloyd	Ass of Pulp, Paper and Board Manufacturers
	E J Smith	SAPPI
	F Hefer	African Products
	E Botes	NTRI
	N P Slabbert	LIRI
	S G Sluttleworth	LIRI

Financing by the WRC and contributions by members of the Steering Committee are acknowledged with thanks.

INDEX

Research into the Treatment of Industrial Effluents with High Salinity and Organic Contents.

Final Report - Period 1983 - 1985.

	Page
Summary	1
1. Introduction	10
2. Report on Some of the Technologies Considered	23
2.1 Ozone	23
2.2 Wet Air Oxidation	24
2.3 Electrodialysis	25
2.4 Ultrafiltration	28
2.5 Carbon Adsorption	31
2.6 Evaporation	32
2.7 Hyperfiltration	32
3. Equipment Used in Tests	37
3.1 Ozone Oxidation	37
3.2 Ultrafiltration and Hyperfiltration - Laboratory Tests	37
3.3 Cross-Flow Filtration	39
3.4 Electrodialysis	40
4. Examination of Selected Effluents	45
4.1 Pulp & Paper Industry	45
4.1.1 Effluent from the Sulphite Pulp Mill at SAICCOR, Umkomaas	45
4.1.1.1 Ultrafiltration of spent and waste liquor using conventional membranes	49
4.1.1.2 Ultrafiltration of E-stage liquor	54

	4.1.1.3	Hyperfiltration of wash-pit liquor	54
	4.1.1.4	Hyperfiltration E-stage liquor	55
	4.1.1.5	Cross-flow microfiltration of sulphite pulp liquor	56
4.1.2	Effluent from Soda Pulp Mill Bleaching Stages		61
	4.1.2.1	Ultrafiltration	61
	4.1.2.2	Hyperfiltration	65
	4.1.2.3	Electrodialysis	66
	4.1.2.4	Carbon adsorption	70
4.1.3	Effluent from the Manufacture of Oxidised Maize Starch Effluent by the Wet Oxidation Method		70
	4.1.3.1	Ultrafiltration	72
	4.1.3.2	Hyperfiltration	72
	4.1.3.3	Electrodialysis	73
	4.1.3.4	Alternative process	75
	4.1.3.5	Concentration of sodium chloride using electrodialysis	75
4.1.4	Effluent from Tanneries		76
	4.1.4.1	Tanneries in S. Africa	76
	4.1.4.2	General Hide Tannery - process and effluent description	76
	4.1.4.3	Sutherlands Tannery Limited Plessislaer, Natal	78
	4.1.4.4	Vleissentraal Koop Bpk. Slagpale Cato Ridge	78
	4.1.4.5	Ultrafiltration	79
	4.1.4.6	Hyperfiltration	84
	4.1.4.7	Cross-flow microfiltration : use on tannery effluents as a pretreatment process	87
	4.1.4.8	Hyperfiltration on permeates from cross-flow microfiltration of tannery effluents	95
	4.1.4.9	Electrodialysis	96

4.1.4.10 Carbon adsorption 97

5. Basic cost structure of treatment processes considered 98

6. Conclusions and Recommendations 99

References 106

Appendix 1. Details of Tannery and Fellmongery establishments 113

Appendix 2. Brief details of the operation, water and effluent quantities at the General Hide Wet-Blue Tannery at Harrismith, OFS 117

Appendix 3. Sutherlands Tannery, Ltd. Pleisislaer, Natal, 1983 124

Appendix 4. Vleissentraal Koop Bpk, Slagpale Curing Store - Cato Ridge, 1983 127

Appendix 5. Basic Cost Structure of Some Advanced Treatment Technologies 134

Figures

1. Scheme A Alternatives 19
2. Scheme B Alternatives 20
3. Schematic arrangement of test rig 38
4. Cross-flow microfiltration experimental rig 39
5. Schematic flow sheet of Ionics electrodialysis stack pack - not including the switch over valves for the EDR mode 42
6. Membrane arrangement 43
7. Flux versus total dissolved solids or lignin 53
8. a-b Permeate flux vs elapsed time as function of temperature 57
9. a-b Permeate flux versus elapsed time 59

10. Relation between molecular size cut off and percent greater than molecular size 63
11. The corn refinery process 71

Tables

1. Recently introduced hyperfiltration membranes 14
2. Analysis of a spent liquor sample 46
3. Analysis of a sample of E-stage liquor from the bleaching process 47
4. Results of ultrafiltration using different membranes from various suppliers 49
5. Analyses of SAICCOR E-stage effluent 54
6. Composition of soda pulp mill bleach stage effluents 64
7. Composition of oxidised starch effluent based on samples used in tests 72
7a. Composition of clear liquor from lime wash liquor 80
8. Analysis of a sample from the ponds at Western Tannery 81
9. Analysis of curing store effluents 83
10. Composition of effluent to ponds at Sutherlands Tannery 85
11. Composition of chrome-wash effluent 86
12. Composition of effluent after the SILFLO Unit - Silverton 87
13. Analysis of samples 89
14. Operations - lime and chrome sections 90
15. Results from run on sample 2 effluent 91
16. Composition of feed and permeate in cross-flow filtration using aluminium hydroxide on nylon hose - sample no.2 92
17. Analysis of effluents (SA Bata, Hanni and Sons, Silverton Tannery) 94

Supplement in separate volume comprising :-

1.	Oxidation of organic matter in effluents using ozone	1 - 21
2.	Wet air oxidation	
3.	Electrodialysis	1 - 28
4.	The use of electrodialysis in the recovery of lignosulphonate from sulphite pulp mill effluents	1 - 12
5.	Carbon adsorption	1 - 13
6.	Membrane fouling in electrodialysis	1 - 52
7.	Identification of ellagic acid in sulphite pulp mill waste liquors	1 - 25
8.	Preliminary examination of effluents from the bisulphite pulp mill SAICCOR, Umkomaas	1 - 35
9.	Batch electrodialysis of SAPPI (Enstra) D_1 + D_2 effluent	1 - 32
10.	Electrodialysis of oxidised maize starch effluent	1 - 21
11.	Cross-flow filtration - A review	1 - 52

SUMMARY

Research into the treatment of industrial effluents with high salinity and organic contents.

1. Introduction

The treatment of industrial effluents with high salinity and high organic content has been examined using a range of techniques such as hyperfiltration (reverse osmosis), ultrafiltration, electrodialysis, adsorption, oxidation by ozone and air and cross-flow microfiltration.

The project outline considered two main processing routes for the treatment of the effluents : Scheme A involved removal of organics using processes such as ultrafiltration, oxidation and adsorption followed by removal of inorganics. Scheme B involved separation of both inorganics and organics to provide reusable water and further treatment of the concentrate by separation for by-product recovery or further concentration for disposal.

The effluents examined in this project were from :-

(a) The pulp and paper industry, essentially from the various stages in the bleaching operations. (Specific studies were also conducted on a sulphite pulp mill spent liquor),

(b) The tanning industry, both wet-blue effluents and total tannery effluents,

(c) The manufacture of oxidised starch by a wet oxidation method in the maize wet-milling industry.

Detailed literature surveys were carried out on oxidation by ozone and by air, carbon adsorption and electrodialysis to assess their suitability and cost effectiveness for treatment of this class of industrial effluents.

1.1 Oxidation by Ozone and Wet Air

Ozonation as a general treatment process for removal of organic compounds was determined to be unsuitable because of cost considerations and the degree of oxidation.

Wet air oxidation is highly capital intensive and only suitable for the treatment of waste waters with a COD of greater than 20 g/l. Thus it is applicable for the treatment of concentrates. The application of this technology, until recently, has been controlled by one organisation. Other organisations have now been examining the process and the Ontario Research Foundation has recently developed a new reactor design which enables the reactions to be carried out at lower temperatures and pressures.

1.2 Carbon Adsorption

Carbon adsorption as a primary treatment was not effective (on soda pulp bleach liquors) because of very high dosages and only moderate removal of organic compounds. In the effluents selected for study (except sulphite pulp spent liquor) a significant fraction of the organic compounds are of low molecular mass and carbon adsorption is unsuitable for these compounds. Studies conducted for the EPA on activated carbon addition to secondary treatment of tannery effluents indicated also that activated carbon has limited ability to bond COD, BOD, TOC, THA, chromium and oil and grease in tannery effluents. Further, there was no apparent correlation between final effluent characteristics and the nature of the tanning operations. This indicated the need to conduct research on an effluent by effluent basis.

1.3 Ultrafiltration

Ultrafiltration tests using a range of nominal molecular mass limit membranes were carried out on various effluents. Rejection of organics in most cases was low because a significant fraction of low molecular mass species is present in these effluents. Ultrafiltration of this class of effluent (except sulphite pulp spent liquor) is unsuitable for good separation of organics from the inorganics. However, its applicability in special cases, as a pretreatment process should not be overlooked if the conventional pretreatment methods are unsuitable for removing fouling contaminants prior to application of a desalting technology.

1.4 Electrodialysis

Electrodialysis of liquors containing both organic and inorganic constituents will not effect separation of the constituents where the organic component is ionised. Even with non-ionised organic materials, some transfer across the membranes can occur. In addition, severe fouling of the anionic membrane can occur in the presence of certain organic materials. Accelerated fouling tests can assist in determining the suitability of the process.

1.5 Application

The above technologies, ozonation, wet oxidation, carbon adsorption, ultrafiltration and electrodialysis are best examined on an effluent by effluent basis.

1.6 Hyperfiltration

Hyperfiltration, especially using thin-film composite membranes, will remove most organics and inorganics at high rejections and the results of this investigation confirm this. The water recovery available from hyperfiltration is dependent on the concentration of ionisable salts in the effluent. The

ionisable salts can be concentrated up to about 70 g/l before the osmotic pressure becomes limiting.

It is in this field that electrodialysis might be considered as a concentrating technology rather than as a demineralizing technology to concentrate beyond the limits achieved by reverse osmosis. However, fouling in concentrates containing organics and certain metal ions may occur and individual examination will be necessary.

1.7 Cross-Flow Microfiltration

Cross-flow microfiltration is an extremely useful separation process (covering the particle size range 0,1 μ to 10 μ) for liquors containing suspended solids and colloids that are normally difficult to separate by conventional filtration techniques.

In some cases a self rejecting dynamic membrane will form often giving some degree of rejection; in others a special layer such as the hydrous oxides of certain metals can be deposited on the base medium to improve filtration specification.

1.8 Evaporation

Evaporation techniques were not considered in this report.

This report presents the results of tests on the various effluents with particular reference to the use of the following technologies :-

(i) ultrafiltration
(ii) electrodialysis
(iii) hyperfiltration
(iv) cross-flow microfiltration and cross-flow filtration with dynamic or regenerable membranes.

2. EXAMINATION OF SELECTED EFFLUENTS

2.1 Pulp and Paper Industry

2.1.1 Effluents from the Sulphite Pulp Mill, SAICCOR, Umkomaas.

2.1.1.1 Ultrafiltration and hyperfiltration

Tests were carried out on the laboratory flat sheet rig using membranes from a number of manufacturers. The results demonstrated that ultrafiltration of the spent liquor can be achieved with a high rejection of lignosulphonates. Saccharides and acetic acid pass into the permeate.

Pilot plant tests were carried out by a firm of consultants on site using commercial modules. The tests confirmed that lignosulphonates can be recovered from the spent liquor by ultrafiltration and that the ratio of sugars and acetic acid to total solids in the starting feed can be increased significantly in the permeates.

Tests on self rejecting membranes laid down by lignosulphonate liquors have shown some promise but more work is necessary.

Hyperfiltration tests have indicated that there should be very little difficulty in concentrating the wash-pit liquor to the same concentration as the spent liquor.

Ultrafiltration of the E-stage liquor is unsatisfactory due to the low TOC rejection. However, this liquor can be concentrated by hyperfiltration to good water recovery with good rejection of constituents at reasonable fluxes. (At over 60% water recovery, flux was 15 l/m^2h when operating at 6 MPa pressure).

2.1.1.2 Electrodialysis

Conventional electrodialysis of the lignosulphonate liquors will not be practicable because of fouling of the anion membrane. The system of electrodialysis using cation-selective and neutral membranes (or other variant with neutral membranes) is not as acceptable as the less energy consuming ultrafiltration process.

2.1.2 Effluents from Soda Pulp Mill Bleaching Stages

2.1.2.1 Ultrafiltration and hyperfiltration

Ultrafiltration does not give high organic removal on $D_1 + D_2$ and E-stage liquors and this is related to the wide molecular mass spread and the large proportion of low molecular mass material in these effluents.

Hyperfiltration, however, does give good rejection of constituents, but fouling tendencies, particularly in the case of $D_1 + D2$ effluents, are indicated. Pilot tests using lime addition, microfiltration and spiral hyperfiltration membranes are presently being undertaken at the SAPPI Enstra mill.

2.1.2.2 Electrodialysis

Electrodialysis of $D_1 + D2$ effluents leads to easy demineralization, but fouling is likely to occur in the long term. Complete separation of organics from inorganics is not achieved. Tests were carried out on site to confirm fouling and these tests will be reported separately. Laboratory tests have indicated that electrodialysis can be carried out with a d.c. energy consumption of about 1 kWh/kg salt removed.

2.1.2.3 Carbon adsorption

Batch tests on a $D_1 + D_2$ bleach effluent were carried out using a number of different activated carbons. Although most carbons were effective in removing colour the use of activated carbon for total organic removal is not economic.

2.2 Effluent from the Manufacture of Oxidised Maize Starch Produced by a Wet Oxidation Method

2.2.1 Electrodialysis

Electrodialysis of this effluent results in good removal of salts. Some organics (10 - 17%) are transported to the concentrating stream. Current efficiencies of 77 - 80% have been obtained. Energy consumption (d.c. energy using the voltage drop across cell pairs only) varied from 0,83 to 0,54 kW/kg salt removed.

The process thus enables reasonable recovery of the organic component in a low salt (500 mg/l) solution. The organic component (starch) can therefore be returned to the process stream.

The electrodialysis process can be operated to produce a concentrated brine. In tests designed to demonstrate the concentration of the brine stream, a concentrate stream containing 170 g/l NaCl was produced. This was achieved at a current efficiency of 90% and an energy consumption of about 1 kWh/kg salt removed.

Since undertaking the above investigation, the manufacturers have abandoned the wet oxidation process and the oxidised starch is now made by a dry process resulting in no effluent.

2.3 Effluents from Tanneries

2.3.1 Ultrafiltration

Ultrafiltration is unlikely to be useful for good separation of organics from inorganics in effluents from tanneries except in special cases because of severe fouling problems and because of the molecular mass spread of the organics in these effluents.

However the technique may be applicable for special cases and in particular effluent streams.

2.3.2 Cross-Flow Microfiltration

Cross-flow microfiltration has been shown to be a useful pretreatment process for the removal of suspended matter (and colloids) before applying hyperfiltration.

In some cases, a membrane can be formed or laid down on the base medium and some rejection of organics can be achieved.

2.3.3 Hyperfiltration

In many of the effluents, after pretreatment by suitable filtration, reasonable fluxes could be obtained during hyperfiltration with good rejection of organics and inorganics.

Water recovery depends on the initial salt concentration and very high concentrations restrict the application of hyperfiltration.

Fouling is general and cleaning procedures must be developed for each effluent.

2.3.4 Electrodialysis

Electrodialysis of tannery effluents was not conducted since the organic constituents will include amino acids which are amphoteric and separation of inorganics from organics will be poor.

2.3(a) Effluents from Curing Stores

The high salt content of the skin curing store effluents makes these liqours unsuitable for treatment either by hyperfiltration or by electrodialysis.

CHAPTER ONE : INTRODUCTION

1.1 The discharge of industrial effluents, unless adequately purified, into the water environment causes a serious problem to the limited water sources in many parts of the country. The necessary technology for the effective treatment of industrial effluents so that they comply with the standards of discharge into the water environment and into municipal sewage systems is, however, not always available. The main types of industrial effluents which cause problems on discharge in this regard are those that contain :-

(a) significant quantities of non-biodegradable organics
(b) toxic or potentially toxic compounds
(c) significant quantities of mineral salts, acids or bases
(d) very high organic loadings.

Of particular importance are those industrial effluents with high salinity and organic contents. These have serious implications, especially at the local level, in terms of the protection of the quality of our water resources. For this reason, the management of these problematic industrial effluents should be undertaken at source. The advantages of the elimination of pollutants in industrial wastewaters at point source are well documented and include :-

(i) Preservation of water quality as the pollutants are not discharged into the water environment either directly or indirectly. This assists greatly in the future implementation of reclamation schemes and the conservation of water resources.
(ii) Improved management of toxic materials, biologically intractable organic materials and mineral salts.
(iii) Increased general environmental effects.
(iv) Increased industrial recycling of water and reuse of treated effluent.

(v) Implementation of the recovery of chemical pollutants and their reuse.

With the steadily increasing cost of water and disposal charges of effluents, along with the future tightening of discharge regulations, the industrial sector is becoming more aware of the need to preserve water by good management and of the necessity to treat effluents in an adequate manner.

The scope for the treatment of these problematic industrial effluents by conventional methods is obviously limited. However, the application of advanced wastewater treatment technology for the control of these effluents is technically feasible using combinations of the following processes :

1.2 Technologies

A brief outline of the capabilities and limitations of the technologies which may be suitable for the treatment of industrial effluents with high salinity and organic contents is given.

1.2.1 Membrane Separation Technologies

Three principal types are reverse osmosis (RO) or hyperfiltration (HF), ultrafiltration (UF) and electrodialysis (ED). A fourth type, which uses larger pore size filtration media than ultrafiltration is known as cross-flow microfiltration (CFM) to distinguish it from other membrane processes. A membrane is basically a selective barrier in that it permits some entities to pass while preventing others from going through.

1.2.1.1 Hyperfiltration

Hyperfiltration is a pressure driven membrane process for separating relatively pure water from solutions containing salts, dissolved organics and colloids. The rejection of

dissolved species, although high, is not complete and depends to a large extent on the size of the species, the chemistry of the membrane and the chemistry of the species.

Hyperfiltration membranes have an upper limit on pressure capability and thus on concentration factor achievable due to osmotic back pressure ; this is approximately 7 - 8% for fully ionised salts. The main processing problem with hyperfiltration membranes is their susceptibility to fouling by insoluble salts and organic compounds. This decreases membrane life and increases operating costs due to the need for adequate pretreatment.

In recent years, hyperfiltration membrane technology has developed rapidly and new membranes with wide pH and temperature limits and good rejection of organics have been developed. Details of these are given in Table 1 and compared to cellulosic membranes. Another innovation is the dynamic membrane which has the advantage of being replaceable in situ. Although still in the development stage, this concept has potential for the treatment of effluents with fouling characteristics.

1.2.1.2 Ultrafiltration

Ultrafiltration is also a pressure driven membrane process although the pressures are lower than that for hyperfiltration. Various sizes of membranes are available (molecular mass cut-offs from 2 000 to 300 000) and the membrane stops particulate matter, colloids, suspensions and large dissolved molecules. Rejection of these species is close to complete.

Ultrafiltration membranes have wide limits on pH and temperature. They are widely applied in industry mainly for the recovery of chemicals from process streams and effluents, e.g. electrocoat paints, whey, size, emulsified oils. Fouling is normally controlled by the application of strong cleaning solutions.

1.2.1.3 Electrodialysis

Electrodialysis is a membrane process in which dissolved ionic impuritites are removed from the water through membranes under the influence of a d.c. electric field. In this process only ionised components are removed or concentrated from the bulk solution. Electrodialysis has found particularly widespread application in the desalting of brackish waters. It has applications also in the concentration of dilute brines e.g. from reverse osmosis and cooling water blow down.

Fouling, particularly of the anion selective membrane, has been a serious limitation of electrodialysis although recently modified membranes with lower fouling rates have been prepared. Cleaning requirements have been reduced substantially by the use of the flow reversal process (EDR), particularly for inorganic fouling.

TABLE 1 : Recently introduced hyperfiltration membranes

Type	FilmTec FT40	FilmTec FT30	Toray PEC1000	Teijin PBIL	UOP PA300	Cellulosic
pH range	-	4 - 11	1 - 13	1 - 12	3 - 10	4 - 8
T limit (°C)	-	60	55	60	45	35
Chlorine	-	Low levels	No	No	No	Yes
Chemical	% rejection	% rejection	% rejection	% rejection	% rejection	% rejection
NaCl	20 - 50	99,5	99,9	99	99,5	99
Ethanol		75	97	61	90	32
Propanol		89	99,5	72	-	54
Phenol		92	99	-	95	0
Acetic acid			86	40	65	7
Oxalic acid			99	90	-	-
Citric acid			-	99	99	-
Urea			85	65	80	24
Ethylene glycol			94	80	-	-
Ethylene diamine			99,5	85	-	71
Methylethyl ketone			98	77	94	29
Ethyl acetate			99	-	95	-
$Ca^{++}Mg^{++}SO_4^{=}$	90					
Sucrose	99					
Glucose	90					

1.2.2 Adsorption Technologies

Adsorption technologies are used for the removal of dissolved contaminants from wastewater by transfer to another phase, normally a solid surface but this may be an immiscible liquid. In the case of ionic species transfer of ions is carried out by ion exchange.

1.2.2.1 Ion exchange

Ion exchange has limited applicability to the treatment of effluents with high salinity and organic contents because of organic fouling problems and the regenerant chemical needs.

1.2.2.2 Activated carbon

Activated carbon adsorption is a well known technology and has many standard applications. Its main use has been as a polisher to remove trace organics. For the treatment of high strength organic effluents, running and capital expenses will be very high.

1.2.2.3 Synthetic polymeric absorbents

A wide range of synthetic polymeric absorbents are now available. Their main advantage over activated carbon is that they can be made more specific and that regeneration by methanol, acids, bases or steam does not involve significant inventory loss as in the thermal regeneration of activated carbon. Their use, however, is also intended for polishing, to remove trace organics.

1.2.3 Thermal Separation Processes

Thermal processes may be used for the recovery of water from wastewater containing dissolved wastes or for the recovery or concentration of the wastes themselves. Evaporative methods have the unique capability for removing all non-volatile

contaminants and for producing highly concentrated solutions. The principal limitation of this process is the energy intensiveness and hence the high operating costs. Fouling and scaling is often evident and with salt solutions, corrosion is a significant design consideration.

The main types, all of which are well established, are thermal evaporation by boiling or flashing and vapour compression. Because of the high cost factor, it is considered that thermal separation processes will be applicable only to the final concentration of low volume, high strength wastes either for final disposal or as a means of heat energy recovery from the combustion of organic materials.

1.2.4 Chemical Oxidation Processes

For high strength organic wastes or effluents containing significant amounts of non-biodegradable material, biological oxidation is inadequate and chemical oxidation methods are applicable. The two main types are wet oxidation and chemical oxidation using ozone.

1.2.4.1 Wet oxidation

Wet oxidation uses air or oxygen under elevated temperatures and pressures to remove organic materials. The degree of oxidation achieved depends on the temperature and the material oxidised. The process works quite well on concentrated wastes and is effective on a wide range of effluents. It is a capital intensive process, however.

1.2.4.2 Ozonation

Ozone is a powerful oxidant and oxidation of any organic contaminants is technologically possible. This oxidation is often enhanced in the presence of certain catalysts. Ozonation of wastewater, low in organic content, to oxidise some of the dissolved organic compounds to less harmful or more

easily removable substances and to oxidise or breakdown organic substances to more biodegradable forms for their removal on biologically active carbon is a viable process in water reclamation. However, because of the low efficiency by which many pollutants are oxidised and the high cost of the oxidant, ozonation is not likely to be applied for the removal of contaminants in effluents with high organic loading.

1.3 The Effluents

Effluents of high salinity and high organic content arise in many industries including pulp and paper, leather, petroleum, chemical, food processing and metal finishing.

The organic pollutants come from either the raw material being processed, impurities being removed from the raw material or by the addition of chemicals during processing. The inorganic pollutants arise mainly from the use of salts, chlorine, acids or alkalis during processing.

1.4 Treatment Schemes

In considering the technologies described in Section 1.2, two main processing routes as shown in Figures 1 and 2 appear to be technically feasible and are described in 1.4.1 and 1.4.2.

1.4.1 Scheme A : Organic Removal Followed by Inorganic Removal (Figure 1)

The effluent treatment stages are :

(i) Removal of organic pollution by ultrafiltration, oxidation or adsorption. Both ultrafiltration and adsorption will produce a low volume effluent (approximately 5 - 10% of the original) containing the organic materials. In some cases this may be reused back in the processes, especially in the ultrafiltration case, but the more general case will be further

concentration by evaporation for final disposal or preferably for use as a low grade fuel.

(ii) Subsequent removal of inorganic salts by membrane separation to produce purified water for reuse and a concentrate. The concentrate, depending on the nature of the inorganic salts, may be further concentrated by evaporation for final disposal or used as a feedstock for precipitation or electrolysis in the case of sodium chloride.

In this scheme, both treatment methods have to treat nearly the full volume of the original stream. The main advantage is that the removal of organics in the first stage will provide a low fouling effluent for the second stage.

1.4.2 Scheme B : Removal of Both Inorganics and Organics Followed by Separation (Figure 2)

The effluent treatment stages are :

(i) Removal of both inorganic and organics by membrane separation into a low volume (approximately 10% of the original) concentrate and production of purified water (90%) for reuse.

(ii) Separation of the inorganics and organics by adsorption or ultrafiltration to produce an inorganic stream for concentration by evaporation, precipitation or electrodialysis and an organic stream for concentration by evaporation for disposal or for use as a low grade fuel.

Alternatively, the concentrate can be treated by chemical oxidation to remove the organics and the resultant inorganic effluent treated as above.

FIGURE 1 : Scheme A Alternatives.

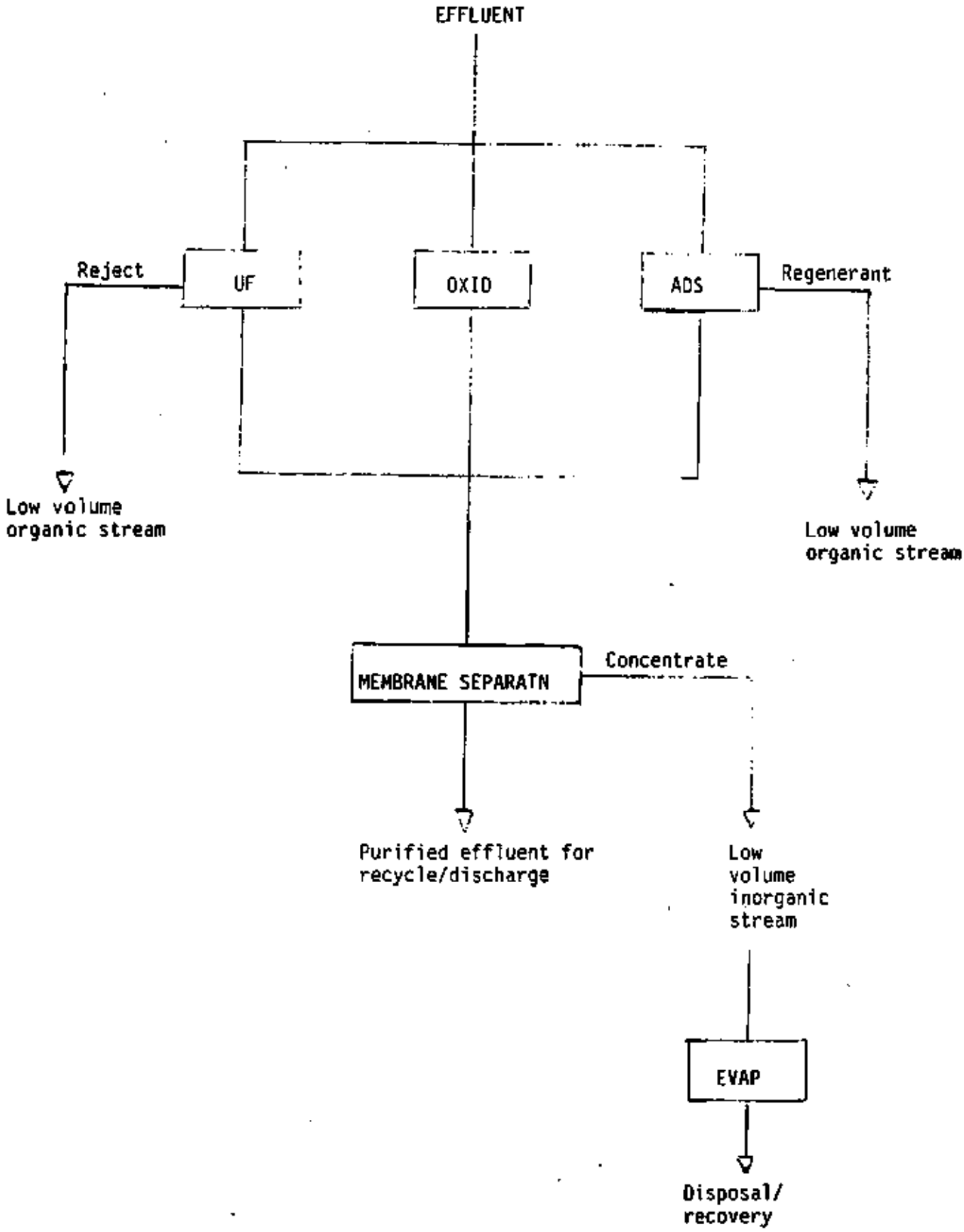
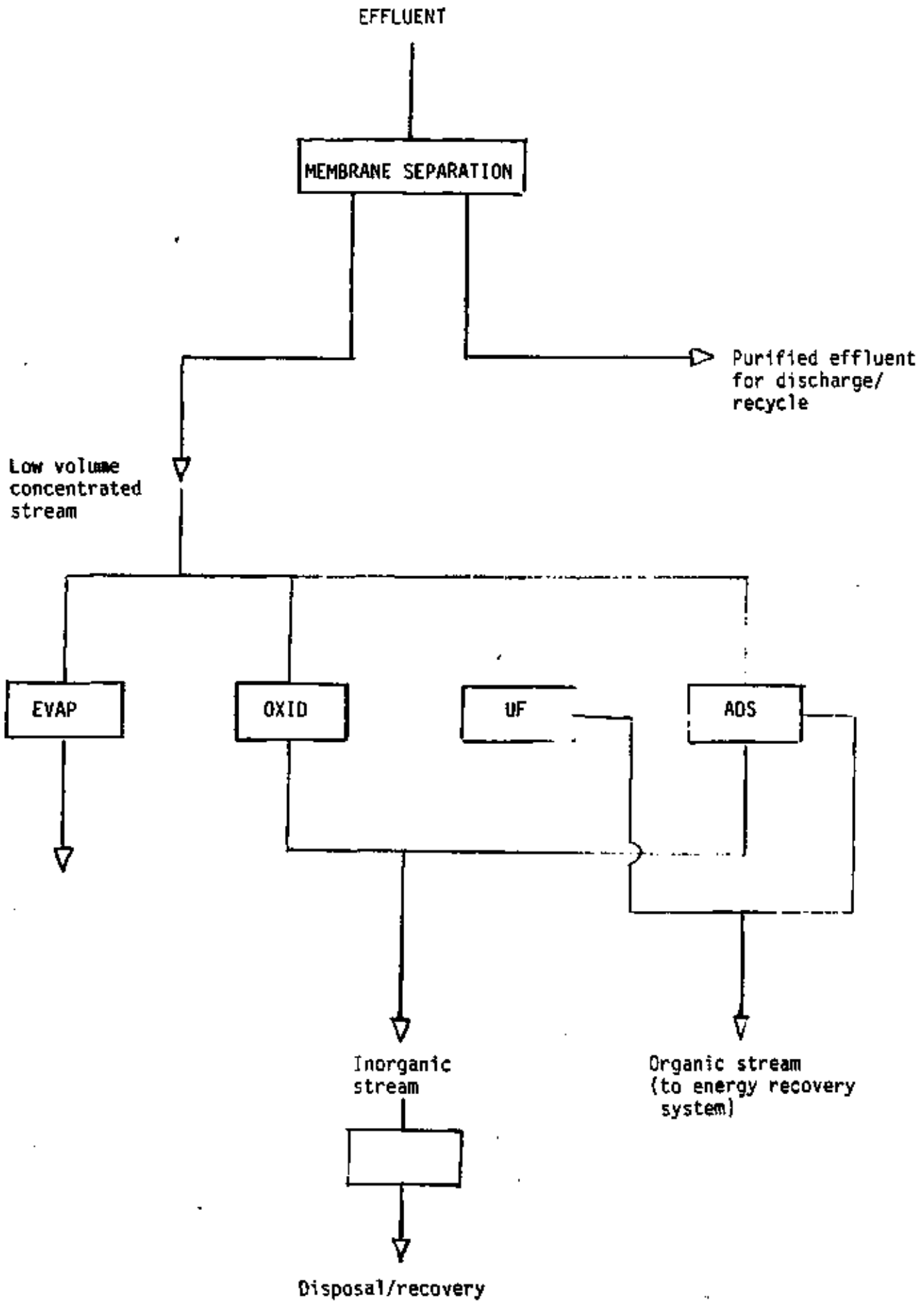


FIGURE 2 : Scheme B Alternatives



The main advantage of this processing scheme is that the second stage treatment is only about 10% of the original effluent volume. If membrane fouling can be controlled or is substantially less in the case of the newer membrane materials, then this will be the preferred effluent treatment scheme.

An alternative processing route may be possible by electrodialysis, which will remove the inorganic salts as a concentrate, leaving the organic in the main effluent. The applicability of this method will be highly dependent on the degree of fouling.

1.5 Water Research Commission Project on "Research into the Treatment of Industrial Effluents with High Salinity and Organic Contents"

At a Steering Committee Meeting on 3rd March, 1983 in the Water Research Commission Offices, Pretoria, consideration was given to investigations on the application of advanced technology, as discussed above, to the treatment of industrial effluents with high salinity and organic contents.

1.5.1 Objective of Investigation

It was agreed :

(i) To determine the technical feasibility of the treatment of effluents with high salinity and high organic content, produced in selected industries, using the separation techniques of hyperfiltration, ultrafiltration, electrodialysis, (evaporation), adsorption and chemical oxidation.

(ii) To determine the most effective and advantageous route(s) in terms of pollution removal and cost effectiveness for a range of effluents in this category.

1.5.2 The Effluents Selected for Study

1.5.2.1 Pulp and paper industry - bleach effluents :

(i) D_1 + D_2 and E-stages - singly and in combination,
(ii) C, E and H stages - singly and in combination,
(iii) black liquor/spent liquor.

1.5.2.2 Tannery effluents

(i) Wet/blue effluents,
(ii) total tannery effluents,
(iii) salt curing effluents and fellmongers effluent.

1.5.2.3 Maize starch industry effluent

(i) oxidised starch effluent.

1.6 This report covers the experimental and survey work carried out on the application of the advanced treatment technologies on selected effluents high in salinity and in organic content.

CHAPTER TWO : REPORT ON SOME OF THE TECHNOLOGIES CONSIDERED

2.1 Ozone

From some experimentation and a detailed literature survey it was concluded that :-

2.1.1 Ozone is a powerful oxidant and oxidation of many organic contaminants is technologically possible. The aqueous phase reactions occuring in a reactor are simultaneous and parallel reactions between the ozone, the decomposition products of ozone and the solutes. Tests have shown that solutes often oxidise at a faster rate when reacting with certain of the decomposition species (e.g. OH radicals) than when reacting directly with the ozone molecule. These species are often less selective to which solute species they oxidise than is ozone.

It is therefore important to understand the relationship of the ozone self-decomposition rate to the system parameters in order to either increase or decrease the ozone decomposition species as the situation may warrant.

Free radical formation (e.g. hydroxyl radical) is increased by increase in pH, increase in temperature, ultraviolet radiation and the presence of metal catalysts.

2.1.2 Various oxidised products will remain in treated water after ozonation.

2.1.3 Ozonation of low COD wastewaters to oxidise some of the dissolved organic compounds to less harmful or more easily removable substances and to oxidise or breakdown organic substances to more biodegradable forms for their removal on biologically active carbon is a viable process in water reclamation.

2.1.4 Because of low efficiency by which many pollutants are oxidised and the high cost of the oxidant, ozonation will be useful only in selective applications for removal of contaminants in effluents with high organic loading.

[To produce 1 kg ozone/h from air approximately 19 kWh of energy is required. To this must be added the capital charges and costs for maintenance, repairs and working capital.]

Ozonation is unsuitable as a general treatment process for the removal of organic compounds. A detailed survey on the use of ozone is given in a separate supplement to this report. (Neytzell-de Wilde, 1985)

2.2 Wet Air Oxidation (WAO)

A survey of the literature has shown that wet air oxidation is a capital intensive process and the volume of effluent treated must therefore be small. For a 4,5 m^3/h plant of a particular design, capital costs (1980) vary between \$1,4 - 2,2 million and operating costs are about \$4,8/m^3.

Wet air oxidation is operated at high temperatures and pressures ; 225 - 330°C and 4 MPa to 20 MPa respectively depending on design and degree of oxidation required.

The process is suitable :

(i) for effluents high in organics and where valuable inorganics can be recovered for reuse. The COD should be high enough to allow the reaction to proceed autogenously (above 20 g/l COD). This will, however, be well below the value which would enable incineration to be self-sustaining (300 - 350 g/l COD),

(ii) for low sludge/effluents/wastewaters containing organic materials which are toxic and/or biorefractory and not

suitable for incineration. The oxidation may be nearly complete or sufficient to modify the noxious chemical so that it is suitable for treatment by other processes.

Two versions of the process have been commercialised ;

a) that based on the tower reactor or Zimmermann process, and
b) that based on the horizontal stirred reactor or Canadian, Wetox process.

The latter process can be operated at lower temperatures and pressures than the tower reactor process and should be considered for specific effuents. Detailed information on the process is given in a separate supplement to this report. (Neytzell-de Wilde, 1985)

2.3 Electrodialysis

Electrodialysis as a unit operation in industrial wastewater treatment has not been used to any extent although the process is recognised as a reliable and economical procedure for the desalination of brackish waters.

An examination of the literature was conducted before applying the process to the effluents under consideration in this project. This is covered in a separate supplement to this report. (Neytzell-de Wilde, 1985). A survey and some experimental work was done on the fouling/poisoning of anion membranes and this is covered, in more detail, also in two separate supplements to this report

(i) Membrane fouling in electrodialysis and
(ii) The use of electrodialysis in the recovery of lignosulphonates from sulphite pulp-mill effluents. (Neytzell-de Wilde, 1985)

2.3.1 Limitations

It has been shown that the major problems which limit greatly the application of electrodialysis as a wastewater procedure are :

(i) The salt concentration of the effluent

Electrodialysis may be used economically for the desalination of water up to 3 000 - 6 000 mg/l total dissolved solids but above this concentration, consideration should be given to the use of hyperfiltration as a separation process.

If the salt concentration is lower than 500 mg/l, electrodialysis may become uneconomical and at high salt concentrations, the permselectivity of the membranes is decreased.

(ii) Wastewater constituents causing membrane poisoning/ fouling and scaling.

The efficiency of the electrodialysis process may be adversely affected if the feed solution contains charged particles, ionised organic molecules or complexes of relatively high molecular mass. These constituents may have an extremely low mobility in the membrane and will, therefore, block or poison the membrane.

Some organic materials, e.g. proteins, amino acids and such like molecules may precipitate on the membrane surface as a result of pH changes and concentration polarisation effects. This also occurs with feed solutions containing colloidal and suspended particles. Scaling may result from the precipitation of salt on the membrane by pH changes, high salt concentrations in the feed solution and concentration.

The acid soluble scales can be removed effectively by reversing the polarity of the electrodes and interchange of the brine and dialysate streams. It is the reversal of hydrogen and hydroxyl ion transfer and the accompanying interchange of pH effects at the membrane surface that results in scale removal.

This process, in which the polarity of the applied d.c. field is reversed and the brine and dialysate streams interchange at regular intervals is termed electrodialysis reversal (EDR). The system will not necessarily deal with organic fouling/poisoning.

(iii) Unchanged or non ionic material

Electrodialysis will not remove co-valently bonded organic or inorganic molecules.

2.3.2 Potential Applications

Electrodialysis is now being used or proposed for use on industrially important separations involving a far wider variety of ions than the alkali and alkaline earths that dominated desalination earlier.

Not only is the process being used for separation of electrolyte from process streams and, in some cases, from wastewater streams, but also for the concentration of electrolytes. Since osmostic pressure is not a factor in electrodialysis, the process has been used for concentrating salt solutions to 20%, and higher, under appropriate conditions.

However, it is difficult to predict the extent that membrane fouling will take place during electrodialysis, particularly of an industrial effluent containing both inorganic and organic materials of a complex nature. Fouling potential of an effluent should, therefore, be investigated on a suitable test

apparatus before attempting to run the effluent through an electrodialysis stack.

2.3.3 Costs

Costs in electrodialysis are heavily dependent on volume treated and amount of salt removed because of the fixed removal capabilities of a given stack of membranes.

2.4 Ultrafiltration

The emergence of ultrafiltration as a viable, practicable separation process has its origins with the development of the first synthetic, high hydraulic - permeability, macro-solute retentive ultrafiltration membrane in 1963 (Cooper 1980).

Today high flux membranes, mechanically rugged and chemically durable and with a capacity to retain molecules as small as, or even smaller than, 500 daltons, and others capable of passing macro molecules as large as 300 000 daltons are available.

2.4.1 Limitations

2.4.1.1 Fouling

A serious technical limitation is the problem of permeation flux depression by solute polarisation. This results in a large reduction in the membrane hydraulic permeability relative to the measured pure water permeation rate. This occurs almost instantaneously on initiation of ultrafiltration. The reduction is related to the concentration of the retained solutes in the feed. Superimposed on this is a further and more serious problem of membrane fouling. This is a slow continuous decline in permeation flux that is substantially independent of feed solute concentration and hydrodynamic conditions.

The fouling process (Cooper 1980) which has variously been ascribed to membrane pore-plugging or to the formation of a slowly consolidating, gelatinous solute-layer on the membrane surface is unpredictable, and appears to vary markedly in severity depending on the composition of the membrane, the nature of retained solutes present in the feed solution, and such other variables as solution pH, ionic strength, electrolyte composition, solution temperature and operating pressure.

2.4.1.2 Fractionation capability

Another limitation is the loss of fractionation capability which occurs in some instances. It may be due to secondary membrane formation via macro solute deposition. This aspect will be demonstrated later.

2.4.1.3 Surface and colloidal phenomena

The importance of the surface and colloidal phenomena is demonstrated by the following :

(i) cationic electrocoat paint dispersions show a much more rapid flux decline than anionic dispersions when ultrafiltered through conventional polysulphone or acrylic membranes.

(ii) certain proteins have a far more depressing effect on the permeability of the more hydrophobic polysulphone membranes than upon the relatively hydrophilic polyion-complex or cellulosic membrane structures.

(iii) polyelectrolytes in the feed lead to the development of significant micro ion rejection by a membrane which would normally display *no* such retention capacity.

The phenomenon has been ascribed to Donnon ion exclusion by a polyelectrolyte polarisation layer. This phenomenon of Donnon

ion exclusion by adsorbed (or pore obstructing) polyelectrolytes applied to porous supports was first utilised in the so-called dynamic membrane reverse osmosis concept.

The formation of such a surface will be demonstrated later.

2.4.1.4 The problem of fouling, or the deposition of boundary layers which cannot be removed by turbulence, is often controllable by cleaning processes so that ultrafiltration processes can be maintained at reasonable rates for long periods. The use of sponge balls or the reversal of flux from time to time has been found to be effective. Operation will normally be within a flux range of 1 - 100 l/m²h at pressures between 100 - 600 kPa and at temperatures up to 80°C.

In spite of these limitations, the process is applied economically in a number of areas including effluents from the textile, dairy and food industries. More recently it has been applied in the tannery industry.

2.4.1.5 Cross-flow microfiltration

In the ultrafiltration process, asymmetric membranes with very small pores are used for the separation of macro-molecular components. When this technique is used with large pore size filtration media, (0,02 micron), also operated in the cross-flow mode, the technique is known as cross-flow microfiltration (CFMF). In this technique the particular suspension (or colloid) is passed over the surface of a filtration membrane under flow conditions favouring the transport of suspending solvent through the membrane, while the concentrated suspension is force-convected across the membrane surface and out of the filtration device (Cooper, 1980 ; Bertera, et al, 1984 ; Groves, et al, 1984 ; Sissou, et al, 1976).

The process is uniquely effective for solid-liquid separations wherein the dispersed solid phase is difficult to remove by

conventional filtration procedures due to the low hydraulic permeability of the resulting filter cake, or where small density differences between suspended phase and the suspended medium make gravity sedimentation or centrifugation inoperative or uneconomic.

The process clearly fits in between conventional filtration techniques (with filtration capability normally of 1 to 40 micron) and ultrafiltration (normally between 0,01 - 0,02 micron). In the system, the thickening of a flux limiting filter cake is controlled by the flow turbulence and the original stream is separated into a large volume of filtrate and a concentrated slurry of solids.

The filtration medium can be modified by additives, e.g. hydrolysable ions and in some cases rejection of macro organic molecules can be obtained.

The process has considerable potential as a pretreatment system prior to hyperfiltration, ultrafiltration and electrodialysis where removal of colloidal and suspended matter is of importance.

A review is given in the supplement to this report (A.E. Orbin, 1985).

2.5 Carbon Adsorption

A brief discussion on carbon adsorption with particular reference to the treatment of a soda pulp bleach effluent is given in a supplement to this report. (Carbon Adsorption, Simpson, A., 1985).

Adsorption is a process whereby a surface retains molecular or ionic species coming into contact with it. The large porosity of activated carbon provides extremely large surface areas per unit mass/volume. The nature of the carbon surface makes

activated carbon particularly useful for adsorbing non-polar hydrophobic species and, in general, organic components which are relatively non-polar or of a relatively high molecular mass are amenable to activated carbon.

As a complete treatment for the removal of all organics from the effluents under consideration, carbon adsorption is not economically feasible.

The application of the technique as a primary treatment step for partial removal of some of the organics could be considered in special cases, but the main application of carbon adsorption is in a polishing step in a treatment scheme.

2.6 Evaporation

Evaporation techniques were not considered in this report because their technology application is relatively straightforward. Effluents containing high salt concentrations and those that are not amenable to other treatment processes should be examined for evaporative treatment.

2.7 Hyperfiltration (or Reverse Osmosis)

Microfiltration, ultrafiltration and hyperfiltration (or reverse osmosis) are basically identical processes and differ only in the size of the particles to be separated and the membranes used. (Strathman, 1981 ; Pohland, 1981 ; Sourirajan and Matsuura, 1982 ; Le and Billingheimer,1985).

Under the driving force of a hydrostatic pressure gradient, some chemical species permeate the membrane while others are more or less completely retained. The term microfiltration is used when particles with diameters in the range 0,1 to 10 µm, are separated from a solvent and other low molecular mass components.

The separating mechanism is based on a sieving effect and particles are separated exclusively according to their dimensions. The membranes used for microfiltration are essentially symmetric microporous structures with pore sizes in the range 0,1 and 10 µm. The hydrostatic pressure differences, used are in the range 10,0 to 200 kPa. (See section 2.4.1.5).

The separation process is called ultrafiltration when the components to be separated are true molecules or small particles not larger than 0,3 µm in diameter, corresponding to the limit of the optical microscope. In ultrafiltration, where the osmotic pressure of the feed solution is in general negligibly small, hydrostatic pressures of 100 - 500 kPa are used. (See section 2.4).

When the molecules to be separated are very small, for example, those with a molecular mass of less then 2 000 - 3 000, the osmotic pressure of the solution becomes significant and cannot be neglected in comparison with the hydrostatic driving force. The separation process is then referred to as hyperfiltration or reverse osmosis.

Since osmotic pressure of the solution to be processed can be quite high and since it has to be overcome by the hydrostatic pressure driving force, the operating pressure in hyperfiltration will be high (2 - 10 MPa).

The membranes used in both ultrafiltration and hyperfiltration have asymmetric structures. The selective 'skin' of ultrafiltration membranes, however, holds well defined pores and the chemical nature of the membrane polymer has only a small effect on the separation characteristics of the membrane.

In hyperfiltration, however, the membrane consists of a more or less homogeneous polymer layer and it is considered that components are transported by a solution diffusion mechanism

(Sourirajan, 1982). The chemical nature of the membrane polymer is therefore of prime importance.

2.7.1 Limitations

Concentration polarisation occurs in all membrane processes. It leads to an accumulation of the retained components and to a depletion of the permeating components in the boundary layer adjacent to the membrane surface.

In the case of hyperfiltration, the low molecular mass material is retained. Due to the concentration increase of the material, the osmotic pressure, which is proportional to the concentration of the solution at the membrane surface, increases. This leads to low transmembrane fluxes for a given hydrostatic pressure driving force. The solubility of the accumulated particles in the boundary layer at the membrane can be exceeded and precipitation occurs, forming a layer on the membrane surface.

Concentration polarisation can never be completely avoided in hyperfiltration or ultrafiltration, but its effect can be controlled to a large extent by the flow distribution of the feed solution at the membrane surface.

Hyperfiltration membranes have an upper limit on pressure capability and thus on the concentration factor achievable due to the osmotic back pressure, this is approximately 7 - 8% for fully ionised salts.

In addition to the above, other processing problems with hyperfiltration membranes include their susceptibility to fouling by organic compounds, susceptibility to oxidation by free chlorine, even at low levels and hydrolysis of cellulose acetate-based membranes.

2.7.2 Pretreatment of Effluent

Pretreatment schemes must include treatment to prevent chemical damage to the membrane such as dechlorination for polyamide type membranes, or pH adjustment to prevent hydrolysis of acetate-based membranes. The major pretreatment requirement, however, is the prevention of 'fouling'.

This includes

(i) membrane scaling such as that caused by calcium carbonate, calcium sulphate, strontium sulphate, barium sulphate and calcium fluoride and deposition of silica and sulphur.
(ii) metal oxide precipitation, for example iron and manganese.
(iii) module plugging by particles greater than 2 μm.
(iv) colloidal fouling by particles less than 2 μm and
(v) organic compounds.

2.7.3 Modules

Four configurations for hyperfiltration equipment have been developed ; the plate, the tubular, the spiral wound and the hollow fibre systems. These systems offer the following membrane surface per unit volume :

Plate module	165 m^2 m^{-3}
Tubular module	335 m^2 m^{-3}
Spiral wound module	1 000 m^2 m^{-3}
Hollow fibre module	16 500 m^2 m^{-3}

The spiral wound and hollow fibre systems are used in the desalination of waters with a low content of solids.

In applications such as in the food industry and in the treatment of effluents with a high content of solids, the tubular membrane system is very useful.

For small installations, particularly in the food or pharmaceutical industry, the plate-and-frame system is often used because the membranes can be readily exchanged.

CHAPTER THREE : EQUIPMENT USED IN TESTS

3.1 Ozone Oxidation

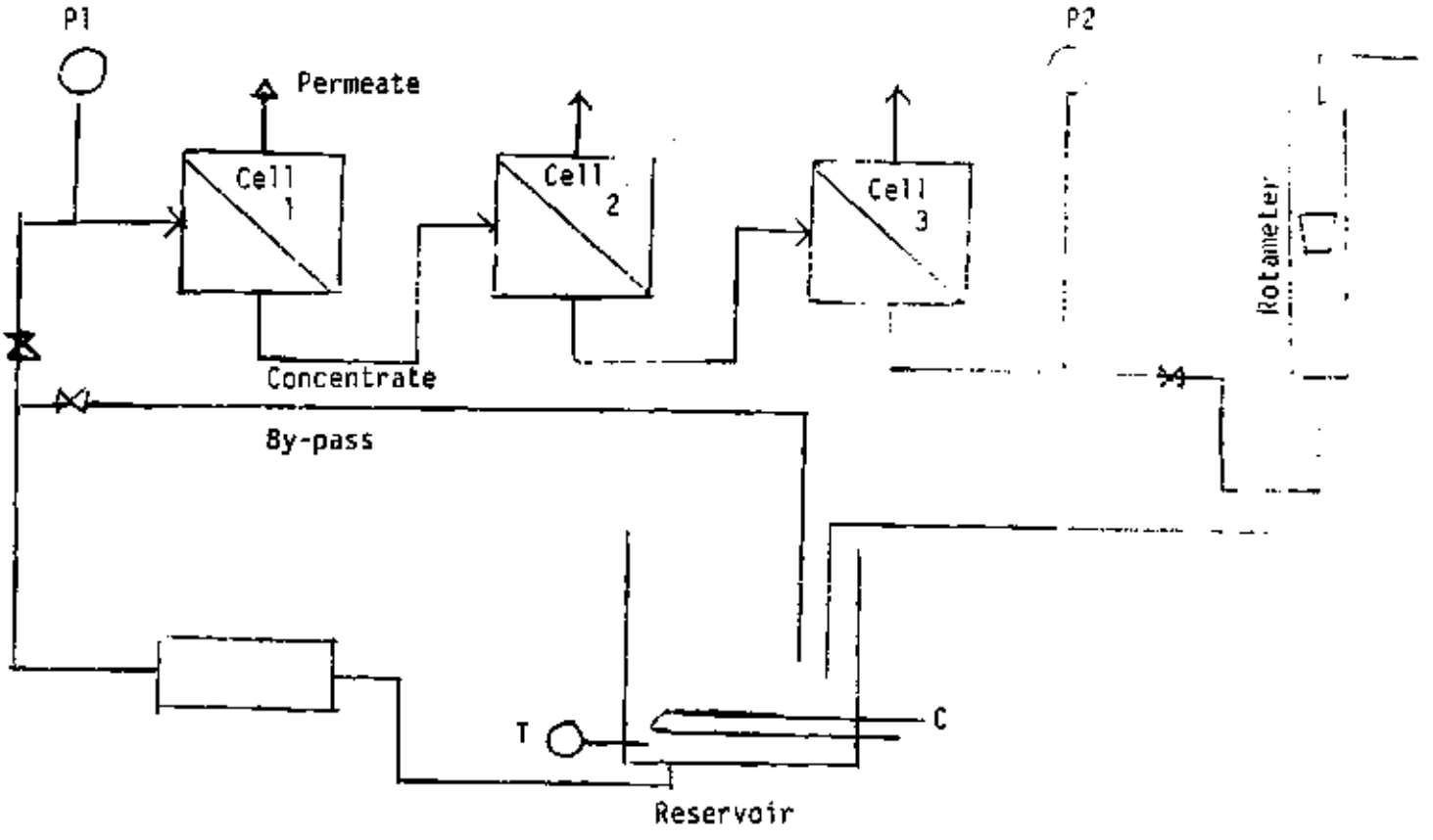
The ozone generator used was a commercial unit (Model LG-2-L2) supplied by W.R. Grace & Co.

It was capable of generating from 5 - 20 g ozone/m^3. With this generator, the strength of the ozone product could be varied by air flow rate and power input.

3.2 Ultrafiltration and Hyperfiltration - Laboratory Tests

Tests were carried out on flat sheet membrane rigs each consisting of three cells in series - allowing tests to be carried out on one, two or three cells per rig as required (Figure 3).

The effective area of the membrane per cell was 0,0011 m^2. The channels in the spacers under the membrane had a cross sectional area of 0,000008 m^2. Thus for a flow across the membrane of only 1 000 ml/min, the velocity was of the order of 2 m/s.



P1) Pressure gauges
P2)

Needle valves
T Temperature gauge
C Cooling coil

FIGURE 3 : Schematic Arrangement of Test Rig

3.3 Cross-Flow Microfiltration

The apparatus is shown schematically in Figure 4.

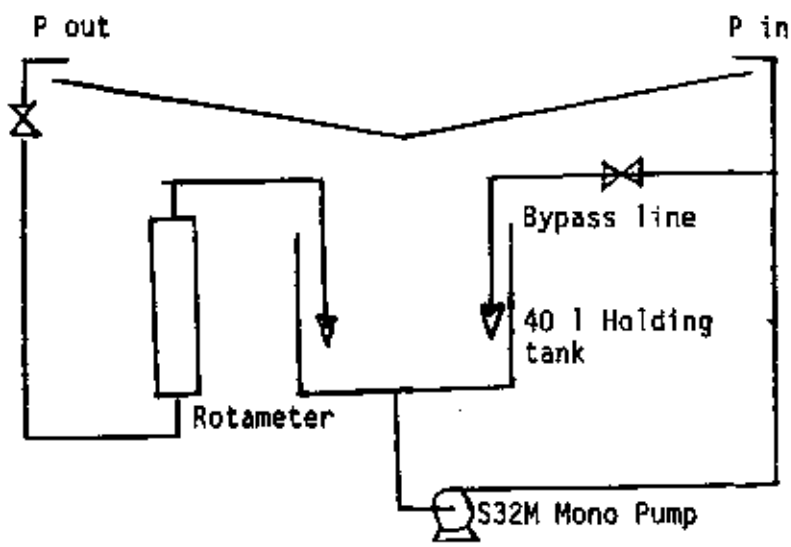


FIGURE 4 : Cross-Flow Microfiltration Experimental Rig

The hose between points P in and P out was a woven hose of nylon or polyester, 12 mm in diameter and approximately 1,94 m long.

The S32 mono pump was run at a speed of 770 rpm.

The circulation velocity through the woven hose in the various experiments was kept at 1,5 - 1,7 m/s.

3.4 Electrodialysis

The unit used in tests was an Ionics Laboratory Stackpack modified for use in either the ED and EDR mode.

The multicell stack is made up of 'tortuous-path' liquid flow channels being bounded on one side by an anion-exchange membrane and on the other side by a cation-exchange membrane to form a compartment or cell. The channels are cut into what are called 'spacers'. Besides furnishing the flow paths, the spacers keep the membranes separated and act as gaskets. The membrane stack, in turn is bounded on one side by an anode and on the other by a cathode.

The stack functions to change the ionic composition of the two liquid streams. Both streams are manifolded in such a way that they flow in parallel through alternating compartments. Upon application of a d.c. electrical voltage between the electrodes, one stream will become demineralized through the loss of anions through the anion membranes and of cations through the opposite cation membranes that bound each compartment through which this stream flows. Conversely, the second stream will become concentrated through pick-up of these ions.

The stream being demineralised is called the diluting stream, and the other the concentrating stream. The sequence, anion-exchange membrane, space, cation-exchange membrane, space is called a repeating section or cell pair.

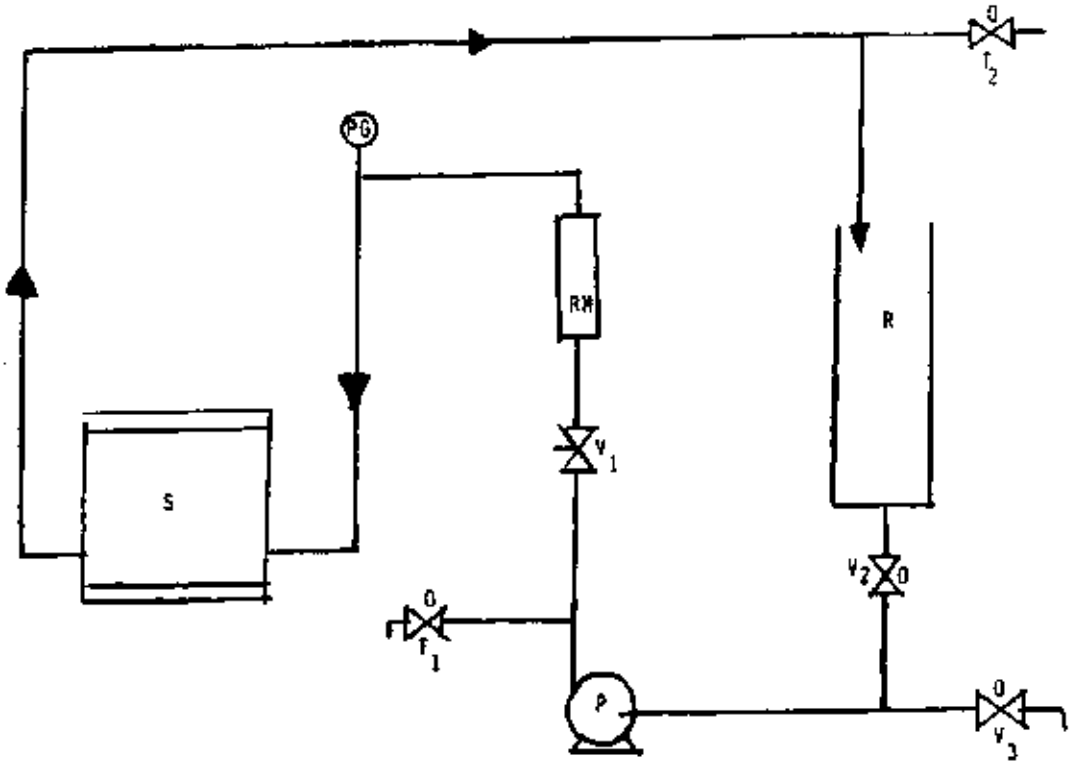
Each electrode is separated from the repeating section portion of the stack by an electrode spacer, cation or anion membrane, and another spacer respectively. Accordingly there are two electrode compartments - one alongside the anode and one alongside the cathode. The electrode compartments are fed by a third stream manifolded into the cell ; this stream receives and carries out the ionic products from the electrode reactions as well as gaseous electrode-reaction products.

A schematic flowsheet of the stackpack is given in Figure 5 and the assembly of the membranes in Figure 6.

Ten cell pairs were used between the electrode compartments. Electrolyte solution was circulated through the electrode compartments at approximately 1,2 l/min at approximately 140 kPa.

Test solution was circulated under similar conditions through the diluting compartments ; and initially test solution or an electrolyte solution, which subsequently became the brine solution, was circulated at slightly lower pressure (130 kPa) through the concentrating compartments. The flow rate was a little more than 30 cm/sec.

The effective area of each membrane was 220 cm^2. The unit was equipped with three reservoirs, each having a capacity of 8 litres. To maximize solvent recovery in the set-up, the initial effluent volume used in the diluting stream was 8 litres, and 2,5 litres in the concentrating steam. In order to examine current efficiency and energy consumption, various methods of operation can be attempted. These are (a) batch operation at (i) constant voltage, or (ii) varying the voltage, to maintain a predetermined constant ratio between current and dilute steam conductivity, so as not to exceed the limiting current. (Solymosi, Aug 1984, Philp, March 1984) ; and (b) continuous operation (feed and bleed).



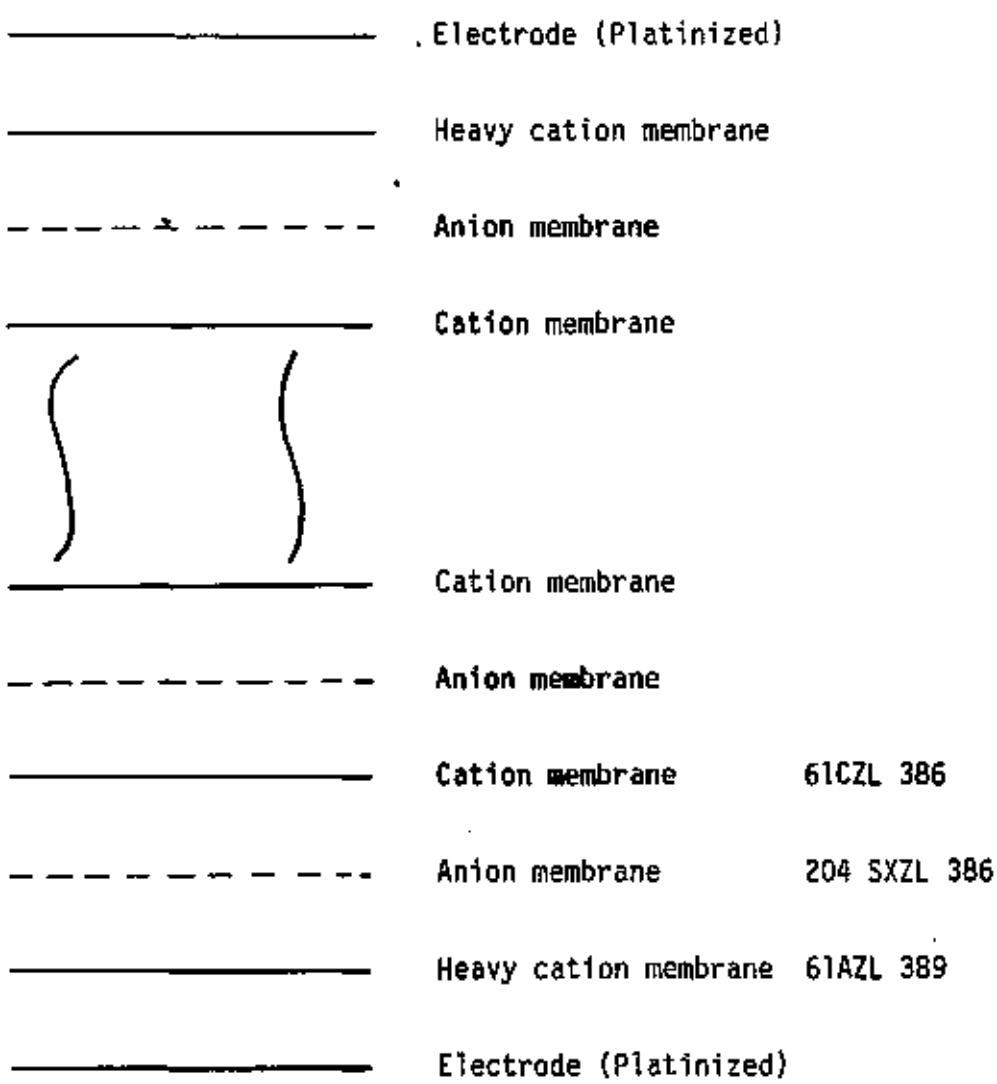
Legend :

V - Valve
R - Reservoir
PG - Pressure Gauge
P - Pump
S - Stack
RM - Rotameter
T - Sample Tap

NOTE : Only one stream is shown

FIGURE 5 : Schematic flowsheet of the Ionics Electrodialysis Stackpack - not Including the Switchover Valves used For the EDR Mode.

FIGURE 6:


Electrode (Platinized)
Heavy cation membrane
Anion membrane
Cation membrane
Cation membrane
Anion membrane
Cation membrane 61CZL 386
Anion membrane 204 SXZL 386
Heavy cation membrane 61AZL 389
Electrode (Platinized)

The demineralization of 8 litres of effluent is not accomplished by one pass through the stack. Multiple passes are needed and this is accomplished by recycle.

In batch operation at constant voltage, the voltage applied at the start of the run must be kept below that value which will cause overheating of the membranes. This value is determined from a safe voltage versus conductivity curve for the particular unit. The chosen voltage can then be kept constant until the effluent has been demineralised to the desired content (say 500 mg/l sodium chloride).

Batch operation, at the limiting current, is conducted so that the predetermined ratio of current to conductivity of the dilute stream is maintained. Initially, however the safe voltage is applied, so that the current is kept below the limiting current. As the effluent becomes depleted in electrolytes, the predetermined ratio is approached and at this point the voltage is varied with the conductivity to keep the current at the limiting value.

In the feed and bleed operation, a batch of liquor is demineralised to the required electrolyte concentration after which feed is fed to the dialysate tank while product is bled off the dialysate return line at the same rate.

CHAPTER FOUR : EXAMINATION OF SELECTED EFFLUENTS

4.1 Pulp and Paper Industry

4.1.1 Effluents from the Sulphite Pulp-Mill at SAICCOR, Umkomaas

The South African Cellulose Corporation (SAICCOR) operates a 1 100 tpd wood pulping plant. The pulping involves the delignification of woodchips by batch-cooking in autoclaves with calcium bisulphite liquors. (Some of the pulping will, in future, be done using the magnesium bisulphite process thereby decreasing the present effluent volume).

A concentrated lignosulphonate/sugar effluent containing over 16% total solids is discharged from the autoclaves via flash tanks at nearly 100°C. This concentrated spent liquor amounts to about 1 440 m^3/d. The remaining liquor, held up with the pulp, is washed out giving a dilute effluent known as wash-pit liquor. This effluent, discharged at 70 - 80°C, contains about 6 - 10% total dissolved solids at peak discharge. The total volume of liquor amounts to about 22 500 m^3/d.

A typical composition of the spent liquor is given in Table 2.

TABLE 2 : Analysis of a spent liquor sample

pH		1,7
Total dissolved solids	g/l	176
Ash	g/l	18,5
Ca^{2+}	g/l	6,5
SO_3 as sulphur	g/l	0,65*
SO_2 as sulphur	g/l	0,31*
SO_2 loosely bound sulphur	g/l	2,24*
Sulphone sulphur	g/l	8,79*
Total sulphur as S	g/l	11,97*
Monosaccharides	g/l	33,6 *
Lignin	g/l	69,2*
Volatile acids - acetic acid	g/l	12,3

* By Tappi Methods

The sugars were determined, routinely by HPLC. It should be noted that the Tappi method (T629 m - 53) for lignin is designed for spent liquors obtained from the pulping of gymnosperm woods. At SAICCOR, angiosperm woods are pulped. The result therefore, is relative only. Further, the method does not precipitate all the lignin and a correction factor is necessary.

A modification was made late in the programme by increasing the precipitant to lignin ratio (Lussi, November 1984). The precipitant, -naphthylamine is carcinogenic and no longer readily available. Investigations are in hand to examine the possibility of using suitable quaternary ammonium compounds such as Hyamine 1622 (di-isobutylphenoxy-ethoxy ethyl dimethyl benzyl ammonium chloride mono hydrate).

In the bleaching section of the plant much of the chlorination stage effluent is recovered by recycle.

For the E-stage, however, approximately one half of the total effluent is sent to drain. This amounts to 150 m3/h (3 600 m3/d).

The analysis of this liquor is given in Table 3.

TABLE 3 : Analysis of a sample of E-stage liquor from the bleaching process

Analysis	Method	Units	
Total dissolved solids		g/l	11,1
Organic dissolved solids		g/l	7,7
Ash		g/l	3,4
Conductivity		mS/cm	7,09
pH			8,45
Calcium		mg/l	36
Sodium		mg/l	2 310
Chloride		mg/l	670
Total sulphur as S		g/l	0,33
Pentoses and hexoses as dextrose	TAPPI	g/l	1,6
Lignin	TAPPI		1,58
TOC	gaseous oxid.	g/l	4,1
Acetic acid	GC.	mg/l	300

4.1.1.1 Ultrafiltration of spent and waste liquor using conventional membranes

(a) Laboratory scale tests

Ultrafiltration tests on both spent and waste liquors were carried out on the laboratory flat sheet rig. The effluent was filtered through kieselguhr to remove fibres, ellagic acid and other particulate matter. (Refer to Supplement "Identification of ellagic acid in sulphite pulp mill waste liquors", Lussi and Neytzell-de Wilde, 1985. Some of the results obtained on different membranes from various suppliers are given in Table 4.

In all cases, there was a dramatic drop in flux compared with the water flux for the membranes. This was then followed by a slower decline due to fouling. Membranes could, however, be cleaned by a water wash to restore effluent fluxes to the initial low level.

These results demonstrated that ultrafiltration of the spent liquor can be achieved with high rejection of lignosulphonates. Saccharides and acetic acid pass into the permeate. Xylose was found to be the main sugar in this effluent.

The lignosulphonates appear to throw down a self-rejecting membrane which effectively alters the 'normal' separation characteristics of the membrane chosen.

Full details of these experiments are reported in the supplement to this report, Neytzell-de Wilde, F.G., "Preliminary examination of effluents from the bisulphite pulp mill, SAICCOR, Umkomaas", 1984.

TABLE 4

Test	Membrane	MWL	Pressure to Cell l kPa	Effluent flux l/m2h	Time of operation min	Analysis g/l							Rejection %					
						Xylose	Glucose	Cellobiose	Lignin	Acetic acid	Total carbon	Ca	Xylose	Lignin	Acetic acid	Total carbon	Ca	Vol. of permeate % of orig. feed
Test 1	Abcor HFM 180 (batch mode)	18 000	400		0 (f)	23,1	5,6	2,3	88,2	12,4	88,9	6,44						
				30,9	30 (p)	22,1	6,1	2,3	24,9	11,8	90,3	4,4	negl	63	negl	43	32	
				16,4	1 089 (c)	27,4	7,6	2,3	129	12,6	117,5	-						
					(p)				32		61,9			74		42		
				17,1	1 607 (c)	30,4	8,1	2,3	155	-	150	8,6						
					(p)				43		69,2			72		54		
					p(bl	29,2	7,5	2,5	28,7	12,5	69,6	5,6	negl		negl			52
Test 2	Abcor HFP 276 (batch mode)		500	1 200 (water)	0 (f)				66	13,5	74,2	7,0						
				83	244 (p)				32	13,2	54,4	5,0		92		26,7		
				46	644													
				37	824 (p)				42	12,37	60,2	5,4		58		46		61
					(c)				100	12,4	111,5	8,2						
Test 3	Abcor HFP 276 (total recycle mode)		500		0 (f)				72	13,7	91,7	7,0						
				88	65 p				42	13,2	57,6	5,0		42		37,2		
				82	780 p				32	12,7	59,4	5,0		48		35,2		
				69	2 135 p				42		57,0			42		33,9		
Test 4	DDS GS61PP (batch mode)	20 000	480		0 (f)	26,6	6,3	2,3	69	-	78,6	6,2						
				3,8	270 (p)	28,6	7,3	2,5	17,2	11,3	43,2	3,8	-ve	73	negl	45	38	
			600	9,8	555 (p)	28,2	7,3	2,5	15	10,3	38,2	2,8	-ve	80	negl	51	50	
Test 5	DDS GS61PP (batch mode)	20 000	1 250		0 (f)	27,7	6,5	-	76,5	14,67	99,5	6,9						
				27	325 (p)	38,6	7,2	-	-	15,71	28,5	1,65	-ve	high	-ve			
				28,8	1 135 (p)	30,2	6,5	-	3,9	15,5	39,0	-	-ve	96	-ve	68	-	
					(c)	29,5	6,5	-	100,01	13,8	110,0	-						
				15,8	1 753 (p)	37,0	6,7				46,0		-ve	high	negl	72		43
					(c)	31,2	6,7		103,0									
Test 6	Millipore PTTK (batch mode)	30 000	400		0 (f)	29,7	6,8	2,3	74	9,6	89,0	6,5						
				47,3	485 (p)	26,8	-	-	29,9	12,4	62,8	5,0	negl	76	-ve	42	32	
					c	26,9	6,4	2,3	135	11,0	107,8	7,4						
				46,4	755 p	-	-	-	43	-	66,8	5,5		72		49	33	32
					c	30,0	7,8	2,3	155	9,9	132	8,2						
					(pb)	28,6	7,4	2,3	31,8	10,4	65,2	5,3						

TABLE 4 (continued)

Test	Membrane	MWL	Pressure to Cell I kPa	Effluent flux l/m2h	Time of operation min		Analysis g/l							Rejection %					
							Xylose	Glucose	Cellobiose	Lignin	Acetic acid	Total carbon	Ca	Xylose	Lignin	Acetic acid	Total carbon	Ca	Vol. of permeate % of orig. feed
Test 7	Osmonics Sepa 50 kDPS (batch mode)	50 000	500	58,2	0	f	27,9	6,9	2,5	70	9,9	75,5	7,0						
				45,5	130	p	28,1	8,0	2,5	25	9,5	53,5	5,7	-ve	64	negl	29	19	
					172	p				26,5	-	54,0	5,5		69		33	28	
						c	21,4	8,0	2,3	85,0	9,8	80,5	7,6						
Test 8	Osmonics Sepa 20 kDPS	20 000	500	-	0	f	-	-	-	36,48	13,73	91,0	-						
				42	305														
				36	425	p	-	-	-	18,39	14,42	52,0	-	-	77	-ve	54	-	
Test 9	Sepa 50 (PS)	1 000	600		0	f	-	-	-	70,48	13,73	91,0	-						
				42-36	300	p				20,16	13,65								
						c				78,10	13,95				74	-ve	-		
				32-26	820	p				19,18	14,39	51,0			78	-ve	55		
						c				85,77	13,65	154,0							
Test 10	Sepa 50 (YP)	1 000	534		0	f	-	-	-	70,48	13,73	91,0							
				13	300	p				15,72	15,73				80	-	-		
						c				78,10	13,95								
				9,8	800	p				17,94	14,90	48,8					-		
						c				85,77	13,65	184,0			79	-ve	52		

f = feed, p = permeate, p(b) = bulk permeate, c = concentrate.

(b) Pilot plant tests

At this stage a group of consultants was ready to undertake tests on site with commercial modules.

Two pilot plant units, a DDS plate and frame system and a PCI tubular system were chosen as the applicable types of module system for this duty. DDS membrane GR61, 81 and 90 and PCI membranes BX1 and BX6U were tested.

The results of these first tests are given in a progress report (Groves, October 1984).

The three most promising membranes were BX1, GR61 and BX6U. Water recoveries prior to diafiltration of 75 - 88% were obtained with a concentrate TDS concentration being over 350 g/l.

Further runs are planned and will be reported elsewhere.

(c) Concentration effect on flux

The pilot plant trials showed a rapid decline of flux value followed by a second decline under batch operating conditions. It was suspected that the latter decline was due to a concentration effect and it was decided to confirm this on the laboratory flat sheet rig. In the recycle operation conditions, on the pilot plant, there was a rapid decline in flux followed by an almost steady state flux as observed in the earlier laboratory tests.

The earlier laboratory tests had not been taken to the high water recoveries that could be achieved easily on the pilot plant units. The effect of a concentration factor of the same magnitude was thus not experienced in the small scale work. The initial severe drop in flux was, however, experienced both in the laboratory rig and on the pilot plant rigs. This is probably due to the nature of

the components of the liquors and is not concentration dependent.

Tests were conducted using GS61PP and GR61PP membranes and samples of spent liquor varying in concentration of non-volatile dissolved solids from 0,84 to 311 g/l. (The GSPP membranes are polysulphone membranes with a nominal molecular cut off of 20 000. The GR61PP membranes are modified polysulphone membranes, modified to give a negative charge. They also have a nominal molecular mass cut off of 20 000).

The results show an initial rapid flux decline on subjecting the membranes to the lignosulphonate liquors. The flux then tends to steady out at a value which appears to be dependent on the concentration of the liquor.

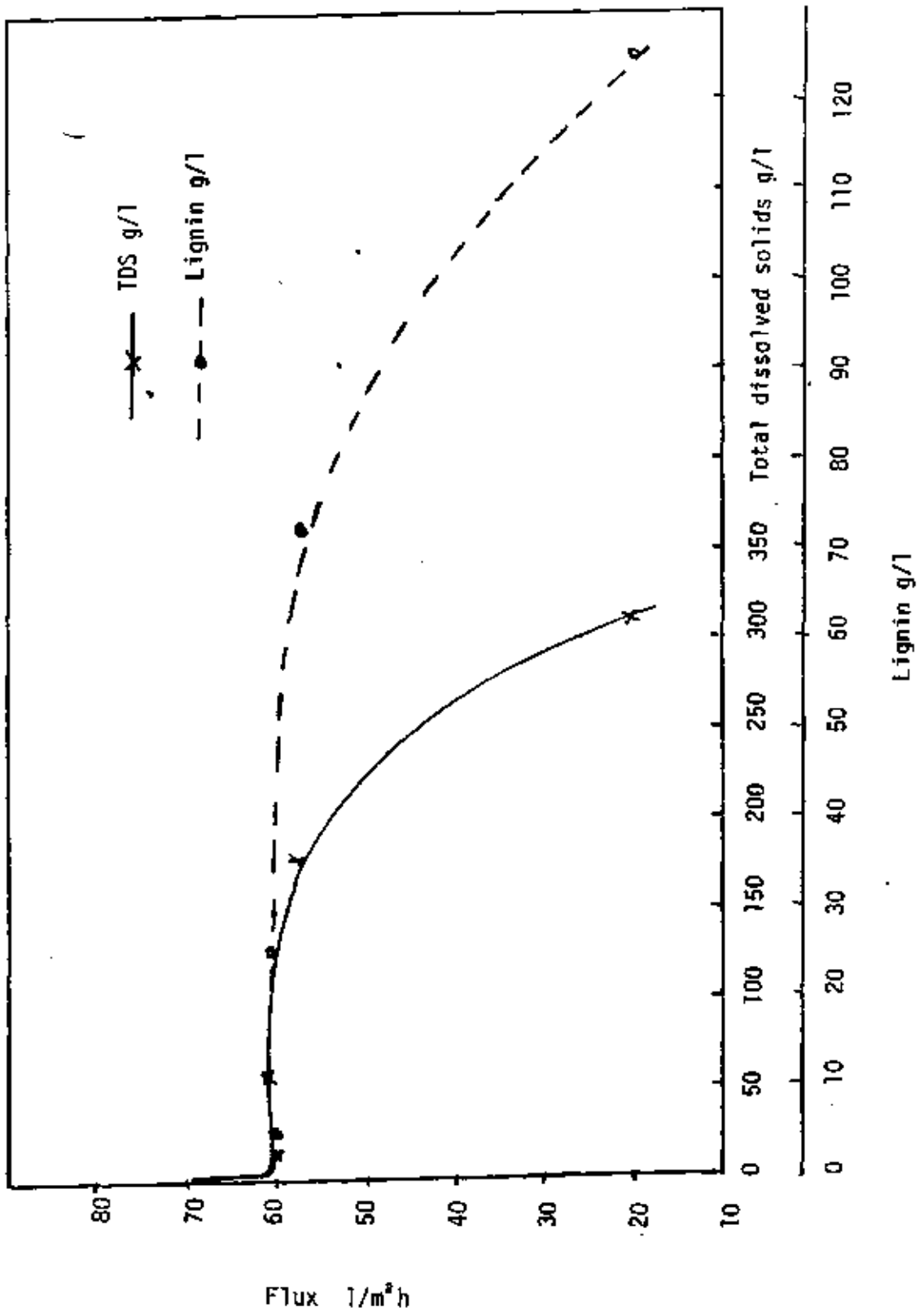
At a non volatile total dissolved solids concentration of over 300 g/l, the flux in this series of tests for the GR61 membrane was about 20 l/m^2h against a flux of 50 - 60 l/m^2h for liquor with a concentration of about 170 g/l. The results are shown in Figure 7 and confirm the findings of pilot plant studies regarding flux trends. It is of interest to note that flux values for the GR membranes appear to be significantly better than those for the GS membranes under similar conditions.

Detailed results are given in a progress report (N-de Wilde, 1984).

All the tests show that lignosulphonates can be recovered from spent liquor by ultrafiltration and the ratio of sugars and acetic acid to total solids in the starting feed can be increased significantly in the permeates.

GR 61 Ultrafiltration

FIGURE 7 : Flux versus total dissolved solids or lignin



4.1.1.2 Ultrafiltration of E-stage liquors

Analysis of an E-stage effluent is given in Table 5. There was little difference in the rejection of TOC component on membranes of widely varying molecular mass limits (5 000 - 50 000). Further, the TOC rejection was low (20 - 32%) and it is considered that ultrafiltration will not be of value in treating this effluent.

TABLE 5 : Analyses of SAICCOR E-stage effluent

pH		8,9
Conductivity	mS/cm	8,1
Total solids	g/l	11,3
Total carbon	g/l	3,6
Chlorides	g/l	0,8
Sodium	g/l	2,5
Calcium	mg/l	22
Acetic acid	g/l	1,2

4.1.1.3 Hyperfiltration of wash-pit liquor
(approximately 6% total solids)

Using seawater type membranes, UOP PA300 and DDS HR98 (similar to Filmtec FT30) at 6 MPa pressure at 27,5 - 28,5°C, good rejection of both total carbon and calcium was obtained (97 - 99%). During batch concentration, rejections remained good and fluxes of above 20 l/m^2h were obtained at 55% water recovery (total solids 136 g/l).

Using a brack water membrane, DDS HR95, at a pressure of 4 MPa and at 35 - 40°C, fluxes above 20 l/m^2h were obtained even at 176 g/l total solids. Rejection of total carbon and calcium was good (98 - 100%).

Clearly, it is feasible to concentrate the wash-pit liquor to the same level of concentration as the spent liquor. The permeate will contain some acetic acid since the rejection of this component is only about 80 - 85%.

4.1.1.4 Hyperfiltration of E-stage liquor

Tests on the laboratory flat sheet rig were carried out on filtered effluent at 6 MPa and at 25 - 40°C, using DDS HR98 membranes. Fouling of the membranes did occur and fluxes dropped steadily over the whole experiment from an initial value of 30 - 40 l/m^{2}h to a value of 12 - 16 l/m^{2}h at an overall water recovery of 65%. Rejection of total carbon was good (over 99%). Acetic acid was partially rejected.

This experiment was followed by a test using a FilmTec SW30-2514 module of 0,56 m^2 in area and carried out at 6 MPa and 25°C. The effluent was pretreated by cross-flow microfiltration using a polyester woven hose.

Fouling was evident in both recycle and batch concentration modes. Initial fluxes (30 l/m^{2}h) dropped steadily. At 65% water recovery a flux of 15 l/m^{2}h was obtained and at 87% water recovery the flux was down to 9 l/m^{2}h. However, rejection of total carbon and sodium was good throughout the test.

Water fluxes could be restored after the membrane was rinsed with water a number of times. If treatment of this effluent becomes necessary more extensive pretreatment would be desirable.

4.1.1.5 Cross-flow microfiltration of sulphite pulp liquors

Preliminary tests have been carried out on the formation of self-rejecting membranes using the cross-flow apparatus described in section 3.3. The apparatus was fitted with a woven nylon hose.

Using spent liquor at a total dissolved solids (TDS) concentration of about 180 g/l and operating at an inlet pressure of 130 kPa and between 25 - 30°C, it was found that permeate flux decreased rapidly to about 4 l/m2h after 42 hours operation in the recycle mode. Reduction in flux occurred similarly in batch operation. However there was a reduction of about 20 - 30% of the TOC content.

Following on from this initial work, further tests were carried out under conditions of constant concentration and constant circulating velocity, varying only the parameters of feed pressure and effluent temperature.

Tests were done at a dilute concentration in the hope that trends in permeate flux or permeate quality at different operating conditions could be better detected.

Diluted wash-pit liquor to give a concentration of about 40 - 45 g/l TDS was used in these tests.

The results are shown in Figures 8(a) and 8(b).

The rate of permeate flux decline is higher for conditions of increased temperature. Pressure of operation (120 kPa or 240 kPa) does not alter the flux decline. Rejection of TOC at or below 50°C was between 20 - 30% but at 80°C rejection appeared to be negative. Permeate fluxes of 50 - 70 l/m2h were obtained over a 10 hour period at circulating effluent temperature of 23 - 37°C. At temperatures of 50°C and higher, the permeate flux declined to between 10 - 20 l/m2h after a period of 5 hours.

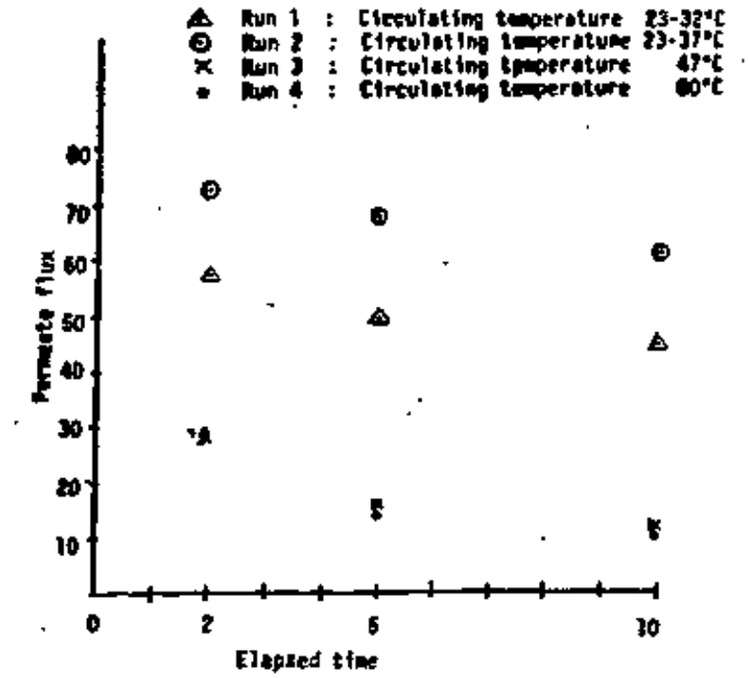


Figure 8a : Permeate flux (l/m²h) vs elapsed time (h) as a function of temperature (feed pressure 120 kPa).

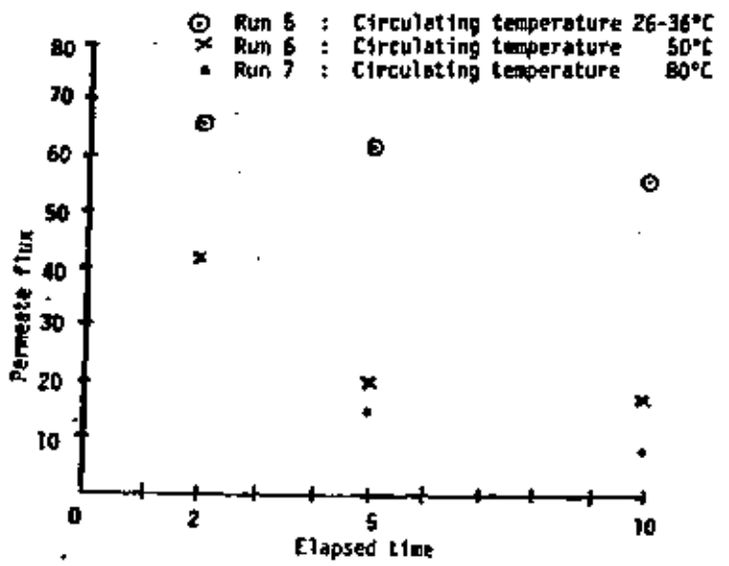


Figure 8b : Permeate flux (l/m²h) vs elapsed time (h) as a function of temperature (feed pressure 240 kPa).

A series of tests at four concentrations (42, 84, 130 and 170 g/l total dissolved concentration) and four temperatures (30°C, 40°C, 50°C and 60°C) were carried out at 120 kPa and a velocity through the hose of 1,6 - 1,7 m/s.

Permeate fluxes obtained at 40°C were similar to those obtained at 30°C for the range of concentrations tested (Figure 9(a) and 9(b)). At an operating temperature of 50°C, severe flux decline occurred for feed concentrations above 42 g/l TDS (Figure 9(c)).

At an operating temperature of 60°C, for feed concentrations of 42 g/l TDS and higher the permeate fluxes declined to below 10 l/m2h within an hour of operation (Figure 9(d)).

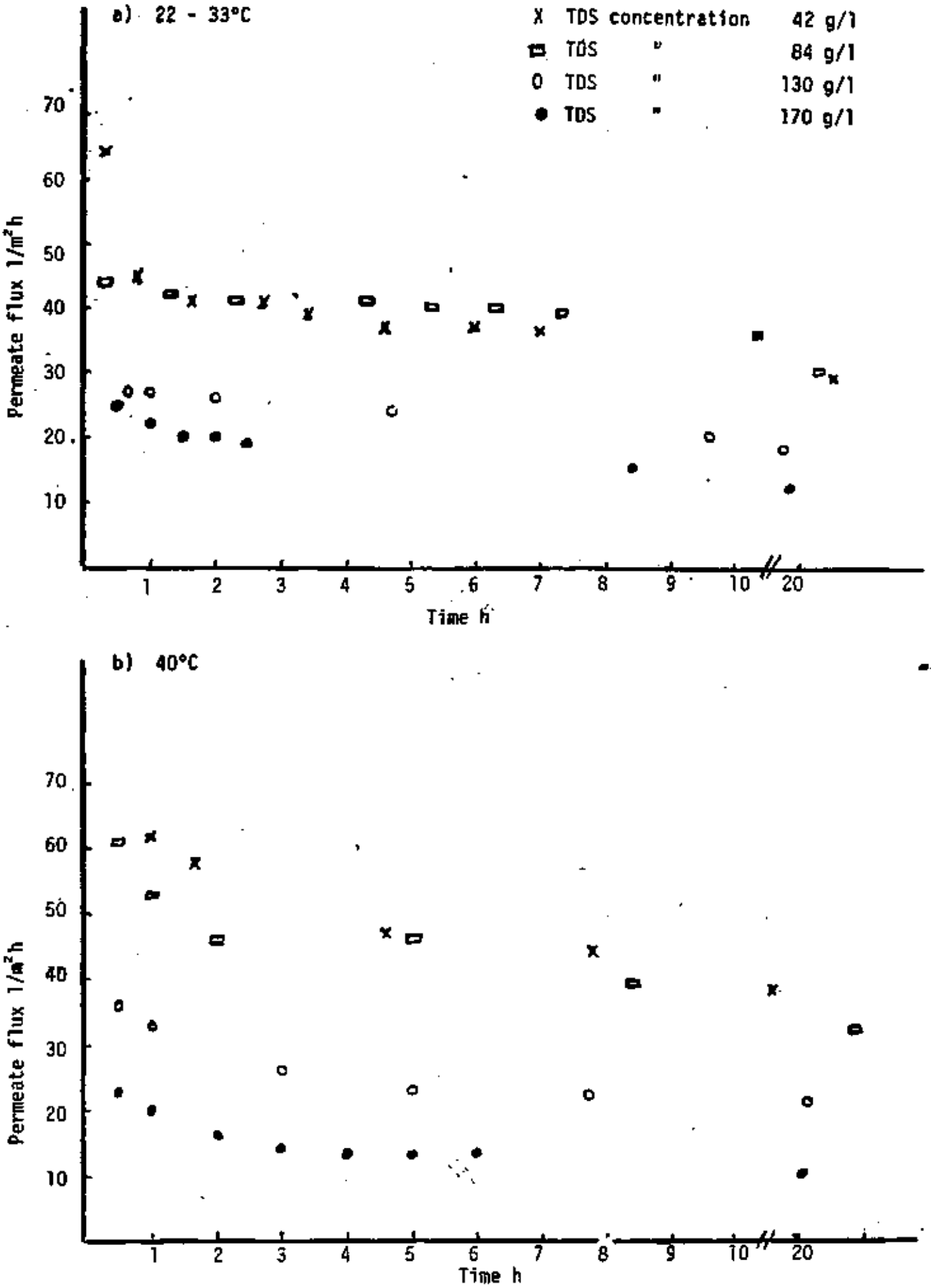
The rejection of TOC varied between 20 - 30% for feed concentrations up to 130 g/l TDS and feed temperatures up to 40°C.

For feed operating temperatures of 50°C, average rejection of constituents decreased to zero for feed concentrations of 130 g/l TDS and higher. No rejection was obtained at any of the concentrations tested for a feed temperature of 60°C.

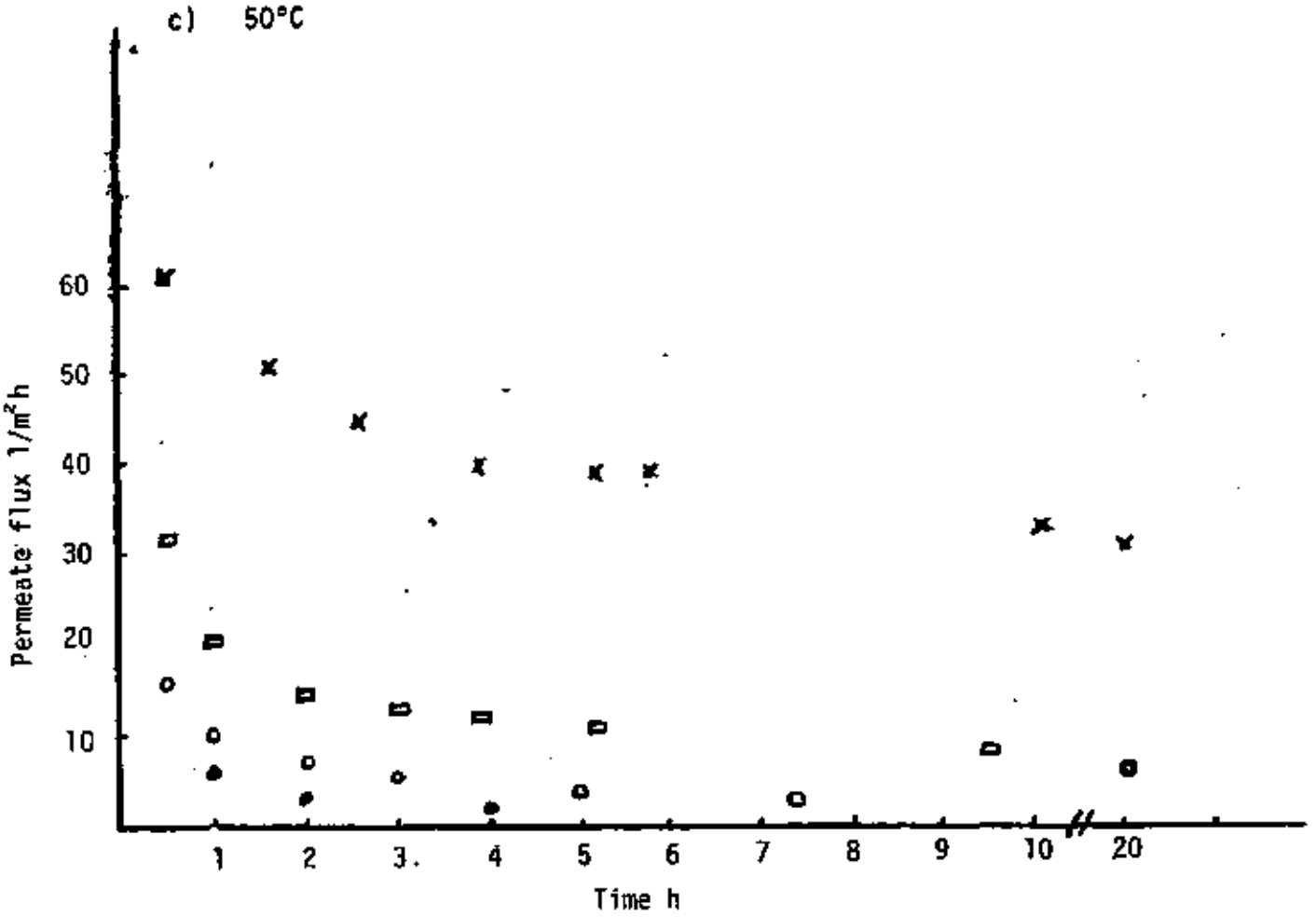
Examination of the permeate flux versus time for feed concentrations of between 42 - 170 g/l TDS at a circulating temperature of 30°C indicates that the permeate flux decreases steeply initially to a low value which is dependent on the feed concentration. Thereafter, the rate of flux decline is similar at the various concentrations. Similar trends have been observed in tests on the ultrafiltration of sulphite pulp mill lignosulphonate liquors. The conditions governing the formation of a self-rejecting membrane are important and a great deal of work requires to be done. Nevertheless there does appear to be potential for the system.

The above results are reported in greater detail in progress reports (Orbin, 6 Sept. 1984, 2 Oct. 1984 and 12 Feb. 1985).

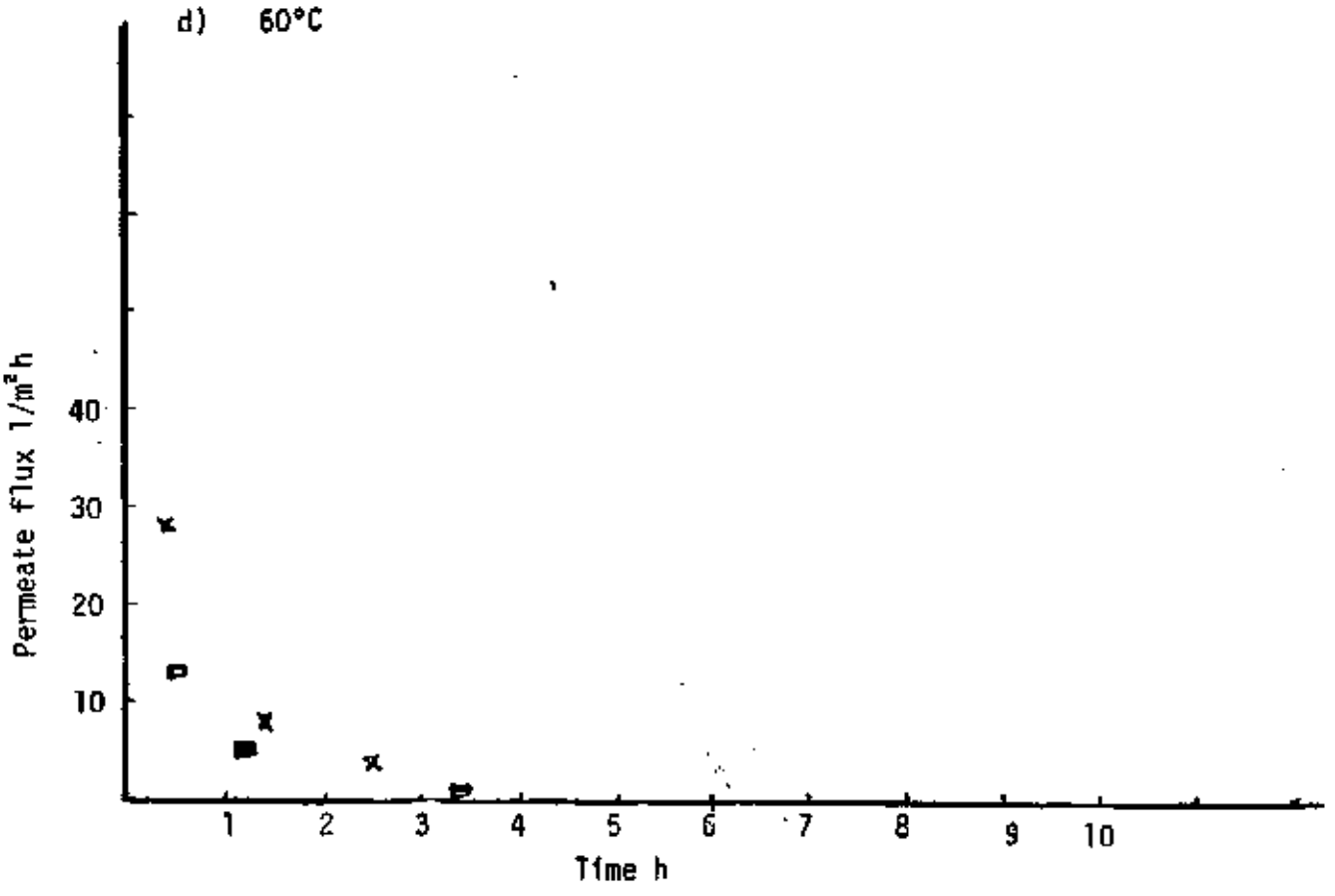
FIGURE 9 : Permeate flux versus elapsed time



c) 50°C


Permeate flux 1/m²h
60
50
40
30
20
10
1
2
3
4
5
6
7
8
9
10
20
Time h

d) 60°C


Permeate flux 1/m²h
40
30
20
10
1
2
3
4
5
6
7
8
9
10
Time h

4.1.2 Effluents from Soda Pulp Mills - Bleaching Stages

4.1.2.1 Ultrafiltration

All effluents were filtered through kieselguhr before ultrafiltration tests.

Samples of effluent from D_1 + D_2, E and D_2 stages at the SAPPI, Enstra mill, and the combined CE and H stages at the SAPPI, Stanger mill were examined by ultrafiltration through membranes of different molecular mass cut off, using the laboratory flat sheet rig. It was found that there was a greater proportion of small size organic molecules in the D_1, D_2 and E stage effluents from the Enstra mill than in the CEH effluent from the Stanger mill. This is shown in Figures 10(a) and 10(b).

A more detailed examination of the C and E effluents from the Stanger mill was undertaken. (The H-stage filtrate is used as a wash in the E-stage and does not therefore constitute an effluent).

Rejection of organics (TOC) from the C stage effluent is poor even for a membrane with a molecular mass cut off of 1 000 (54%). The rejection of organics from the E-stage effluent, however, was higher ; a membrane with a molecular mass cut off of 1 000 gave a rejection of 82% and a membrane with a molecular mass cut off of 10 000 gave a rejection of 67%. This effluent has a larger molecular size fraction than the E stage from the Enstra mill.

Table 6 gives the approximate composition of some of the liquors tested.

FIGURE 10

Relation between molecular size cut off and precent greater than molecular size

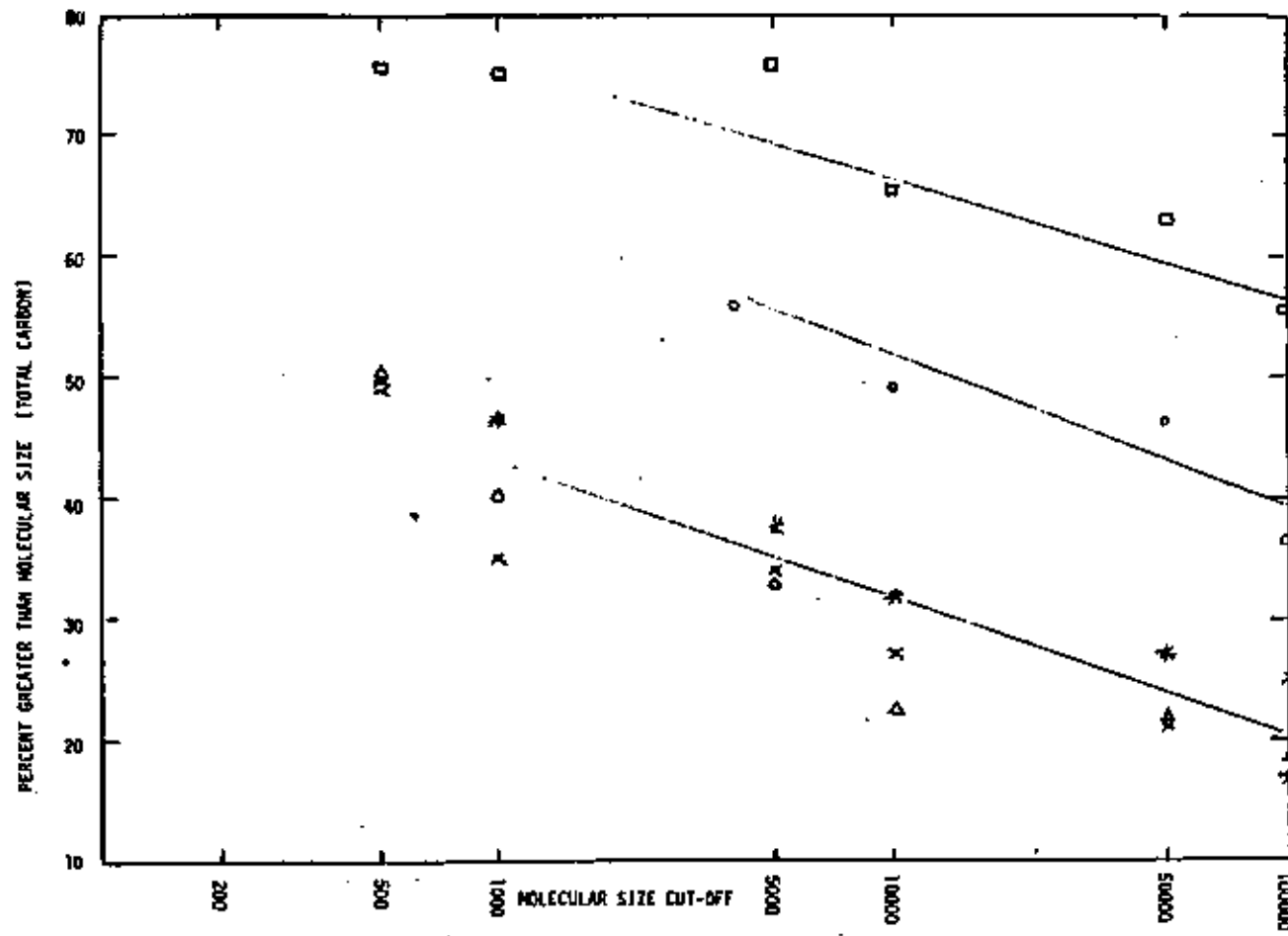
a) Total carbon

b) Polyphenols

▭	CEH, stages	- Stanger mill
*	E-stage	- Enstra mill
Δ	D_1 + D2 stages	- Enstra mill
x	D_1 + D2 stages (second sample)	- Enstra mill
o	D_2 stage	- Enstra mill

FIGURE 10:

a)


PERCENT GREATER THAN MOLECULAR SIZE (TOTAL CARBON)
MOLECULAR SIZE CUT-OFF

b)

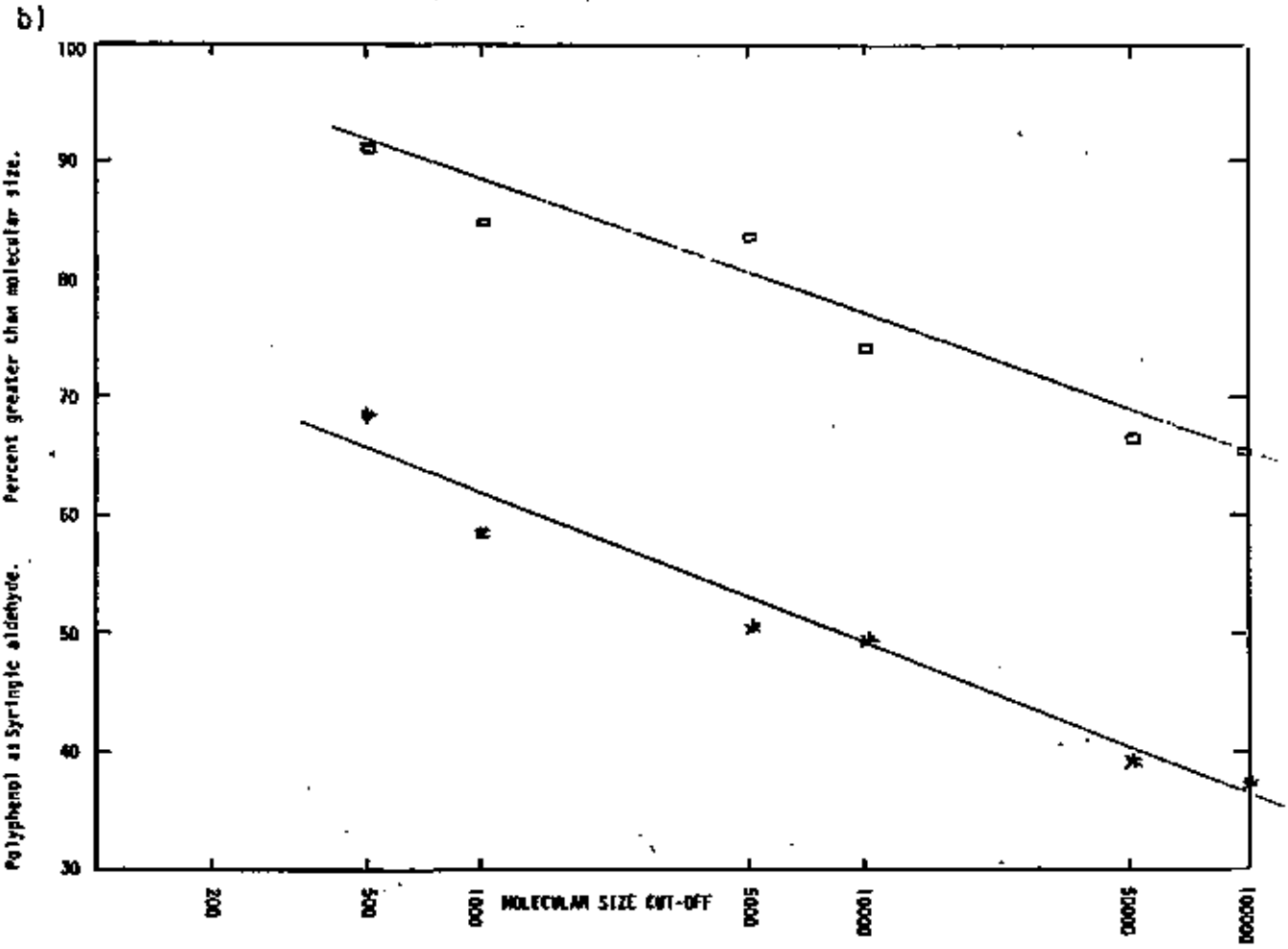

Polyphenol at Syringic aldehyde.
Percent greater than molecular size.
MOLECULAR SIZE CUT-OFF

TABLE 6 : Composition of soda pulp mill bleach stage effluents (Average values for a particular sampling period)

	Total organic carbon (TOC) mg/l	pH	Conductivity mS/cm	Na^+ mg/l	Cl^- mg/l
$D_1 + D_2$ (Enstra)	630	5,4	3,85	590	1 030
D_2 (Enstra)	140		1,67	225	400
E (Enstra)	300	11,0	2,38	500	400
C (Stanger)	360	2,5	3,82	360	990
H (Stanger)	350	7,1	2,54	730	980
E (Stanger)	1 230	10,9	3,01	1 010	800
CEH (Stanger)	560	6,8	3,15	760	970

The effect of the treatment of the effluent with lime before ultrafiltration was examined. The effluent samples were treated with 1 g CaO/litre and stirred at 60°C for 1 hour. The liquors were then centrifuged and filtered and the clear liquor treated with CO_2 to reduce the calcium concentration (pH 9,3). The CO_2 treated liquors were centrifuged and the clear liquors subjected to ultrafiltration tests. The fixed addition of lime to the different effluents (Enstra $D_1 + D_2$, E, Stanger CEH, E, C, H), gave rejections of TOC of between 17 - 37% depending on the effluent stage, except for the E-stage (Enstra) which gave only 5% rejection.

Total rejection by lime followed by ultrafiltration was similar to rejection by ultrafiltration on the untreated effluent.

In general, ultrafiltration of this class of effluents is unsuitable for good separation of organics from the inorganics.

(Detailed information on the above tests is given in progress report, Neytzell-de Wilde, 1985).

4.1.2.2 Hyperfiltration

All samples were filtered through kieselguhr before hyperfiltration tests. Tests were conducted using two types of seawater membranes UOP PA300 and DDS HR98. The flat-sheet laboratory rig was used in these tests.

(a) Stanger mill, E stage

Due to the low osmotic pressure of the Stanger extraction stage effluent, relatively high initial fluxes were obtained (70 - 80 l/m^2h) which dropped slowly to above 30 l/m^2h after 90 hours total recycle. During batch concentration, fluxes of 32 - 42 l/m^2h were obtained at 72% water recovery. Rejections remained at 97 - 100% on all constituents throughout the tests. Hot water rinses were successful in restoring distilled water fluxes to between 82 - 88% of their original. Effluent fluxes were partly restored to 76 - 84% by this procedure.

(b) $D_1 + D_2$ stage (Enstra)

Reasonable fluxes were maintained due to the low solids content of the effluent. After 60 hours under total recycle mode fluxes were still above 20 l/m^2h. During batch mode, 77% water recovery was achieved with fluxes of 15 l/m^2h.

Rejections of components remained above 97%. Normal cleaning procedures did not restore fluxes effectively ; this effluent exhibits fouling tendencies.

(c) E stage (Enstra)

Rejection on components remained high during both recycle and batch concentration operation. During batch concentration, 72% water recovery was achieved at which stage flux was approximately 35 l/m^2h. Flux could be restored to a high level by hot water rinses.

4.1.2.3 Electrodialysis

The molecular size spread of the various bleach stage effluents is wide. For a $D_1 + D_2$ effluent from the Enstra mill, only 25% of the total organic carbon (TOC) had a molecular mass greater than 50 000 and only 50% was greater than 500 (see Figure 10).

It is generally accepted that organics which are not dissociated, for example sugars, do not cause problems with membrane fouling in electrodialysis. With dissociated organics, provided the molecular mass is less than or equal to a few hundred, there will, in general, be no anion-exchange membrane fouling problems. However, for other dissociated molecules, there will be either slow penetration or coating of the membrane with resultant increase in resistance (fouling).

It was, nevertheless, decided to electrodialise the $D_1 + D_2$ - effluent since the sodium chloride content could be reduced quite easily to 500 mg/l and the brine stream increased in concentration. (The latter aspect is discussed elsewhere in this report : section 4.1.3.5).

4.1.2.3(a) Laboratory Tests

The tests carried out on SAPPI bleach effluent are described in detail in a supplement to this report "Batch electrodialysis of SAPPI (Enstra) $D_1 + D_2$ bleach effluent", Solymosi, A., 1985, and in progress report, Neytzell-de Wilde, F.G., 1983.

These tests have shown :-

(i) a large proportion (18 - 48%) of the organic carbon moves out of the diluting stream, and good separation of organics from the inorganic content is not possible. (Since organics present in other bleach effluents such as C and E are similar in character, it is likely that separation of organic and inorganic constituents will be unsatisfactory also, and no electrodialysis tests were done on these effluents).

(ii) The current efficiency during electrodialysis of the effluent is lower than that for sodium chloride of the same conductivity under the same conditions

Voltage V	Current efficiency	
	Sodium chloride soln	Bleach effluent
30	93,6 - 95,2	68,4 - 72,2
20	96,0 - 100	73,2 - 86,2

The time required to demineralize the bleach effluent is nearly double that required to demineralize a salt solution of the same conductivity.

The organic molecular size spread in the bleach effluent is wide. This could cause the electrolyte species in the effluent to move more slowly due to the large slow moving organic molecules obstructing the path of the electrolytes in the bulk solution and at the membrane surface.

(iii) Water recovery for all the runs was between 73 - 75% ; this is satisfactory since the experimental set up the maximum possible was 76,2%. Again, however, water

transfer was higher in the bleach effluent than in sodium chloride solution of equivalent conductivity.

Voltage V	Water transfer per cell pair (into concentrating stream) ml/F	
	Salt solution	Bleach solution
30	0,42 - 0,53	0,54 - 0,58
20	0,36 - 0,51	0,54 - 0,69

(iv) Energy consumption - energy required to remove 1 kg of sodium chloride.

The following values were calculated :-

Voltage applied	kWh/kg sodium chloride removed	
	sodium chloride soln	bleach effluent
30V	1,25 - 1,29	1,64 - 1,77
20V	0,67 - 0,78	0,82 - 1,04
Adjusted to limiting I	0,60	0,87

The estimated range of costs of d.c. energy to electrodialyse the bleach effluent to a fixed mineral content (500 mg/l) from 2,9 g/l (assuming d.c. energy at 5,6 c/kWh) is as follows :-

Voltage applied	cents/m^3
30V	26,7 - 28,7
20V	13,3 - 16,9
Adjusted to limiting I	14,1

(v) The effluent was studied in a flow through accelerated fouling test apparatus and there were indications that resistance of the anion exchange membrane increased, even in the electrodialysis reversal mode (EDR). It was considered desirable, therefore, to conduct tests on site in a small unit to confirm the laboratory tests and this, in fact, was undertaken. The preliminary information on such tests is given in section 4.1.2.3(b)

4.1.2.3(b) Electrodialysis of bleach effluent on site

The laboratory electrodialysis stack was erected at the SAPPI site in order to carry out longer term tests to check fouling and to show the difference between electrodialysis of

(i) Raw but filtered bleach effluent ($D_1 + D_2$),

(ii) Bleach effluent treated with resin to remove the large molecular fraction,

(iii) Bleach effluent treated with lime, to remove portion of the organics, and followed by filtration through a cross-flow microfiltration unit.

Tests will be reported by SAPPI in due course.

4.1.2.4 Carbon adsorption

The treatment of a $D_1 + D_2$ bleach effluent by activated carbon was investigated and the results are fully reported in a supplement to this report. (Carbon Adsorption, Simpson 1985). Although most of the carbons tested were effective in removing colour, it is not economic to use carbon on high volume effluents for their complete treatment. Carbon adsorption should be used only as a polishing step in any treatment scheme.

4.1.3 Effluent from the Manufacture of Oxidised Maize Starch Effluent by the Wet Oxidation Method

A typical flow diagram for a plant processing corn (maize) by wet milling is shown in Figure 11.

The African Products, Meyerton Mill, operates according to such a diagram. A stream of purified corn starch is reacted in Modification Tanks with sodium hypochlorite and caustic soda to produce an oxidised starch. In the process some carboxyl and carbonyl groups are introduced into the starch molecule. Excess hypochlorite is destroyed with SO_2.

The effluent from this process is difficult to deal with biologically because of the high salt content which goes with the high organic content.

This is a low volume effluent, only 100 m^3 per day (maximum) or 300 m^3 per week containing about 8 - 12 g/l Na^+ present with chloride and sulphate, and about 7 - 8 g/l TOC, mainly starch.

If this effluent could be treated by techniques to separate the starch from the inorganic constituents effectively, it may prove economic to process the starch in one of the other processes in the mill.

The composition of the effluent is shown in Table 7.

FIGURE 11:

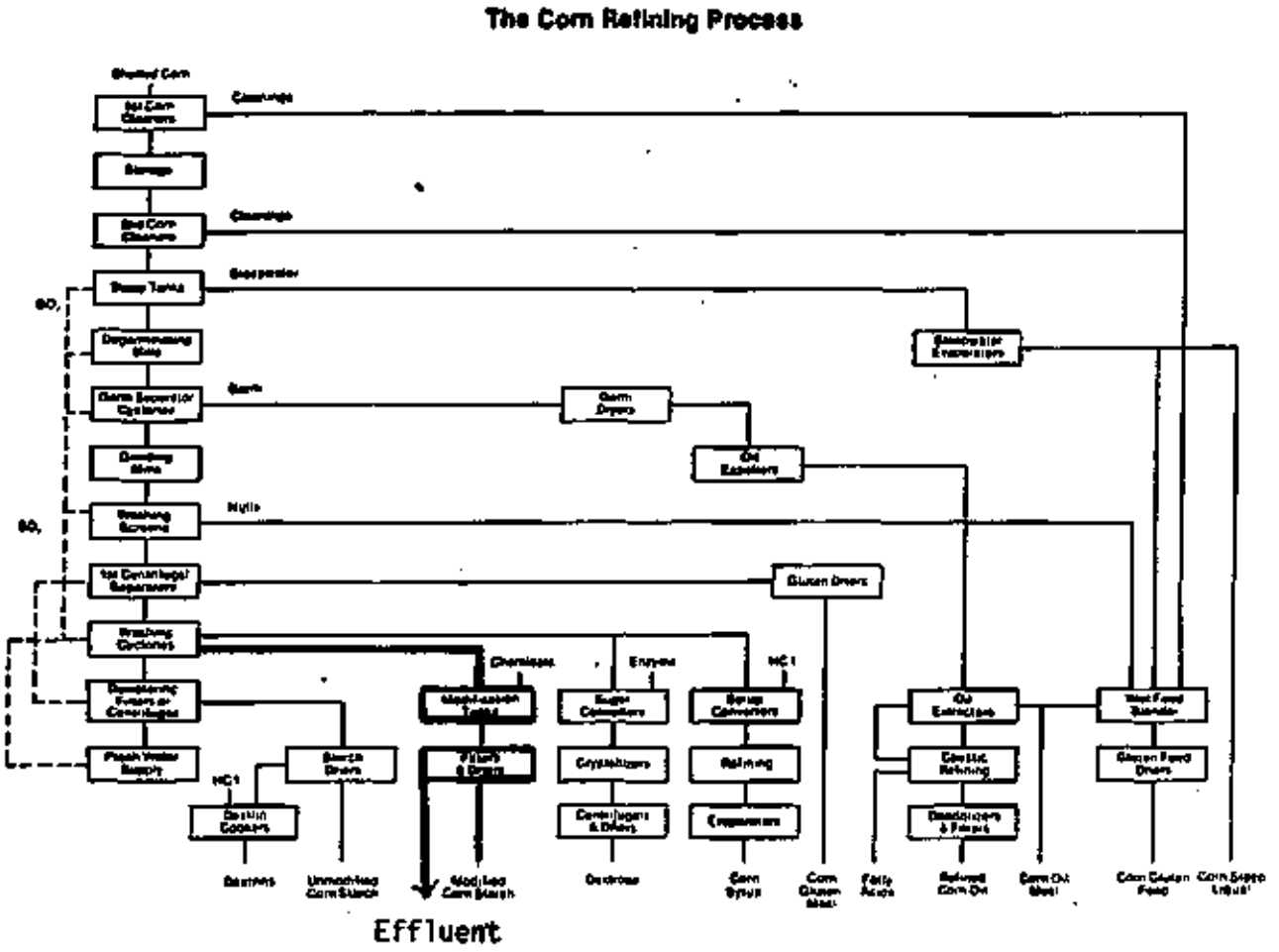


TABLE 7 : Composition of oxidised maize starch effluent based on samples used in tests

pH		4,5 - 6,1
Conductivity	mS/cm	32,8 - 46,6
Na^+	mg/l	7 800 - 11 500
Cl^-	mg/l	9 600 - 18 000
$SO_4^=$	mg/l	240 - 4 400
TOC	mg/l	3 300 - 7 800

4.1.3.1 Ultrafiltration

Using Berghof BM100 and BM50 membranes at 500 kPa, the rejection of organics of the two membranes was similar (58% TOC) and not sufficiently high to make ultrafiltration attractive.

4.1.3.2 Hyperfiltration

A DDS seawater membrane (HR98) and a UOP seawater membrane (PA300) were used in tests at 6 MPa and between 26,5 - 27,5°C. In an experiment conducted under total recycle conditions flux declined from 60 - 70 l/m^2h to 20 - 30 l/m^2h after 40 hours operation. Rejection of TOC, Na^+ and Cl^- was high (96 - 99%).

During a batch concentration step, flux decline with increasing concentration of the feed was sharp. Rejection on total carbon remained above 99% throughout. Rejection on chloride and sodium dropped to 91 - 92% for the UOP membrane at 70% water recovery, at which point concentration of the sodium in the feed had increased to about 23 g/l. Despite this high concentration, the DDS HR98 sea water membrane maintained a rejection of 98% on NaCl at 70% water recovery.

Flux decline with increasing concentration during the batch concentration step was severe. This is to be expected, not only due to fouling, but also due to the increase in osmotic pressure.

Although good rejection of both organics and inorganics was obtained, the process does not offer recovery of the valuable starch component and it was decided, therefore, to examine treatment by electrodialysis.

4.1.3.3 Electrodialysis

Electrodialysis of a solution results in two streams ; one with a high salt content and the other with a low salt content (concentrate and diluent streams respectively).

When the organic component is essentially a non-electrolyte, the electrodialysis unit can be operated so that the organic component will tend to remain in the low salt content stream. Oxidised maize starch has some carboxyl and carbonyl groups and the carboxyl will confer a negative charge. This unfortunately, would assist movement of the oxidised maize starch molecule during electrodialysis.

The results of a series of electrodialysis experiments that have been carried out on different batches of oxidised maize starch effluent and on salt solutions of similar ionic content as the effluent are given in a supplement to this report : "Electrodialysis of oxidised maize starch effluent", Solymosi, A., 1985).

The tests have given the following results :-

(i) Current efficiency (from voltage measured across the cell pairs only)

	Sodium chloride solution at 20 g/l.	Oxidised maize starch effluent.
At constant voltage (20V)	81,5 - 91	77,4 - 86,0
Voltage controlled to limiting i	81,8 - 85,5	80,1

(ii) Energy consumption

	kWh/kg salt removed	
At constant voltage (20V)	0,68 - 0,74	0,74 - 0,83
Voltage controlled to limiting i	0,50 - 0,58	0,54

(iii) Water recovery was about 65% ; the maximum possible with the experimental set up was 76%.

(iv) There was a movement of total organic carbon across into the concentrate stream of 10 - 17%.

(v) The demineralization at limiting current density, requires 10,53 kWh/m^3 of effluent with an initial conductivity of 34 mS/cm at 25°C. This amounts to R0,69 per m^3 of effluent (demineralized to 500 mg NaCl/l ; d.c. energy cost at 5,6 c/kWh).

Electrodialysis of this effluent thus enables satisfactory separation of the inorganics from the organic content of the effluent. The viability of the process would depend on the use that can be made of the organics in the dialysate. Further concentration of the brine in this and other cases may be desirable and this aspect is covered in section 4.1.3.5.

4.1.3.4 Alternative process

The above tests have demonstrated potential of the three membrane processes, ultrafiltration, reverse osmosis and electrodialysis for the treatment of the oxidised starch effluent. However, the manufacturers have re-examined the process and have introduced a dry oxidation procedure, in which no effluent is produced.

The wet milling process produces other liquors such as steep water, from which it may be possible by membrane processes to recover valuable constituents and save water which need not necessarily be evaporated. This aspect should be examined.

4.1.3.5 Concentration of sodium chloride using electrodialysis

Using the laboratory Ionics Corp. Stackpack Unit, tests were conducted to demonstrate the feasibility of using electrodialysis for concentration of brine streams.

In developing a method to give the best results in relation to

a) highest sodium chloride concentration (170 g/l),
b) highest current efficiency (90%),
c) relatively low power consumption (1 kWh/kg sodium chloride removed),
d) high water recovery (90%),

it was found necessary to minimise any leakage from the diluate to the concentrate compartments by sealing off the concentrate entry ports of the membrane spacers. The above results were obtained with entry ports sealed. (Solymosi, April 1985).

In considering concentration of this nature, it will be necessary to restrict the application to such brine streams that are free from those constituents which are likely to cause fouling.

4.1.4 Effluent from Tanneries

4.1.4.1 Tanneries in S. Africa

A list giving some details of tannery and fellmongers establishments is given in Appendix 1.

4.1.4.2 General Hide Tannery - process and effluent description

A short description of the process and effluent arisings (1983) at the Harrismith tannery is given in Appendix 2a and the proposed future effluent streams is given in Appendix 2b.

The effluents as shown in Appendix 2 are separated into two main steams, the lime section effluents and the chrome section effluents, each amounting to about 90 - 100 kl/day for the processing of 1 000 hides per day.

Treatment of these effluents by membrane processes was not satisfactory. Fluxes were low for both ultrafiltration and hyperfiltration and the high salt content of these effluents would result in poor water recovery by hyperfiltration. (Section 4.1.4.6).

A group of consultants was commissioned in 1983 to undertake a study on the treatment of the effluents. The streams in operational sequence are summarised from Appendix 2.

Operation	Number		Volume of effluent involved kl/d
Lime Section			
Soak	1		33,0
De-hair			
Liming	2		17,6
Wash	3		33,0
Fleshing	4		
Chrome Section			
First wash	5		20,9
Second wash	6		20,9
Delime			
including bate	7		13,1
Wash	8		20,9
Pickle, chrome			
tan & basify	9		-
Wash	10		20,9
		Total	180,3

Examination of effluent analyses indicated that the effluents should be separated into the following :

A] Numbers 1, 5, 6, 7, 8 ; Total volume = 108,8 kl/d
B] Numbers 2, 3 ; Total volume = 50,6 kl/d
C] Number 10 ; Total volume = 20,9 kl/d

A] is a relatively 'clean' effluent
B] comprises the high pH, high organic content effluents and
C] is the only acidic effluent.

Combination of the settled liquor B] with the settled liquor C] results in further significant precipitation of organic matter. Binnie and Partners have tested the procedure in their pilot plant at Harrismith. The settled liquor is then aerated to remove sulphide and the sulphide free liquor is then treated with ferric chloride and the remaining solids are removed in a clarifier or by means of a dissolved air unit.

In the latter case, however, fresh water is used to produce the aerated water since clear effluent causes too much frothing in the air dissolving tank.

The proposed treatment scheme for removing the bulk of the organic matter (COD) from the lime and chrome section effluents B] and C] by auto precipitation followed by clarification appears to work well and results in a sludge with good drying properties. (Sludge from the lime section alone does not produce a sludge with good dewatering properties).

It was decided therefore to examine the effluent represented by A] (i.e. effluents naturally low in organic content) and the effluent from the pilot plant (i) before the addition of ferric chloride and (ii) after the addition of ferric chloride.

For the examination it was proposed to consider pretreatment by cross-flow microfiltration, followed by reverse osmosis.

4.1.4.3 Sutherlands Tannery Limited Plessisilaer, Natal

A short description of this tannery is given in Appendix 3.

4.1.4.4 Vleissentraal Koop Bpk. Slagpale, Cato Ridge

A short description of the curing store is given in Appendix 4.

4.1.4.5 Ultrafiltration

a) Sutherlands Tannery - Pietermaritzburg

A sample of effluent from the flume leading to the aeration ponds gave disappointing results on ultrafiltration. A membrane with 5 000 molecular mass cut off was used but rejection of TOC was only between 40 - 45%. 'Protein' was rejected to about 70%. (N-de Wilde, 1983).

b) General Hide Tannery - Harrismith

The lime effluent (from operations 2 and 3 Appendix 2) was treated by physical methods to remove the massive amounts of suspended solids. The clear liquid was treated by ultrafiltration using membranes with molecular mass limits (MML) of 1 000, 5 000 and 10 000. Fluxes were extremely low for the 1 000 MML (1 l/m^2h). The other membranes gave fluxes between 21 - 38 l/m^2h after operation of only just over 2 hours.

Rejections of protein of about 60% and TOC of 90% was shown for the 5 000 and 10 000 MML membranes. Sulphide rejection was low. Analysis of this liquor is given in Table 7a.

TABLE 7a : Composition of clear liquor from lime wash liquor

pH	12,2
Total dissolved solids	61 280
Organic solubles	43 450
Inorganic solubles	17 830
Sulphate	1 850
Sulphide	6 600
Sodium	5 200
Calcium	1 750
Total organic carbon	20 000

(concentrations in mg/l)

Ultrafiltration is not likely to be a useful process for good separation of organics from inorganics, but the low rejection of sulphide may prove to be useful in recycle of this constituent where the remaining small molecular constituents are unlikely to interfere with the dehairing process (Neytzell-de Wilde, 1983). At the time of these investigations, the Steering Committee was not keen to follow up this separation. Nevertheless, it is recommended that work be carried out in this area, and in particular, in the use of cross-flow microfiltration, with and without the use of preformed membranes on the filter medium.

It is suggested that, with preliminary treatment and the development of suitable 'dynamic' membranes, a process could be developed to yield a permeate rich in sulphide and low in organics for reuse in the unhairing sections. Such a process is allegedly in use elsewhere and work on membrane processes with this separation in mind has been described. (Kleper, 1979 ; Drioli, 1980 ; Drioli and

Cortese, 1980 ; Drioli and Molinari, 1984).

c) Silverton Tannery

Because of the low organic content of the effluent from the SILFLO unit no ultrafiltration tests were carried out.

d) Western Tannery

Samples taken from the ponds at Western Tannery were treated by ultrafiltration using membranes with MWL of 10 000, 18 000 and 100 000. Rejection of organics was negligible ; molecular size was probably very small due to degradation in the ponds. The high salt content makes this effluent unsuitable for reverse osmosis treatment as well. An analysis of a sample is given in Table 8.

Table 8 : Analysis of a sample from the ponds at Western Tannery

pH	9,4
Conductivity mS/cm	98,2
Total dissolved solids	75 000
Organic solubles	4 400
Ash	70 600
Chloride	36 590
Sodium	28 400
Sulphate	2 235
Total organic carbon	870
Inorganic carbon	1 250

All concentrations in mg/l.

e) Curing Store - Vleissentraal, Cato Ridge

Although there were plans at the curing store to install a SILFLO Unit followed by a vapour compression evaporator to treat the highly saline effluent (see Appendix 4), it was considered desirable to examine the potential of the membrane processes for the treatment of such effluents.

Three effluent samples were taken :

(i) a sample from the salt washing plant,

(ii) sample of the fluid draining onto the salt treatment area,

and (iii) a sample from the evaporation pond.

Analyses of these samples are given in Table 9.

TABLE 9 : Analysis of curing store effluents

	Sample 1 (salt washing effluent)	Sample 2 (curing store skin drainage)	Sample 3 (effluent ponds)
pH	3,5	6,9	7,1
Conductivity mS/cm	329	440	97
TDS g/l	230	307	55
Organic solubles g/l	25	15	4
Inorganic solubles g/l	205	292	51
Free and saline ammonia mg/l	24	125	47
Chloride (Cl^-) g/l	111	175	32
Sodium (Na^+) g/l	65	110	20,5
COD mg/l	23400	31600	6700
OA mg/l	127	1200	49
Protein (Folin) mg/l	92	3800	224
TOC mg/l	294	5559	307
IC mg/l	6	16	17
TC mg/l	300	5575	324
$PO_4^=$ mg/l	22	13	10

The two effluent streams from the curing operation (skin drainage and salt washing) are extremely high in sodium chloride content, (over 20% in the case of the skin drainage stream). The effluent pond liquor appears to have been heavily diluted and no separation tests were conducted on this material. In any case, separation of organics and inorganics would probably be unsatisfactory because the organics would be degraded after storage in the pond.

Electrodialysis of the effluents would not achieve any separation nor would concentration by hyperfiltration be possible because of high salt concentration. Ultrafiltration of the curing store skin drainage liquor showed that about 50 - 60% of TOC was rejected and about 80% of the protein. However, this was achieved at very low flux and rapid fouling of the membranes.

Separation of organics from the inorganics in the salt washing liquors was low (16% rejection of TOC). Membrane separation processes for separation of inorganics and organics are not satisfactory for the effluent. (Neytzell-de Wilde, Feb. 1984)

In general, the clean separation of organics from inorganics in the tannery effluents is unlikely to be successful because of the wide molecular size range and fouling problems. However, the technique may be applicable for special cases and in particular effluent streams.

4.1.4.6 Hyperfiltration

a) Sutherlands Tannery

Hyperfiltration tests were carried out using DDS HR98 seawater membranes at 5 MPa. Operating in the total recycle mode, flux remained steady for the first 7 hours at

40 - 50 l/m2h then declined to 26 - 31 l/m2h during the next 7 hours. Rejection of inorganic and organic components was good (97 - 100%).

During batch concentration, fluxes dropped to 25 - 29 l/m2h at 50% water recovery and further to 16 - 20 l/m2h at 75% water recovery.

Rejection was good for all components at 97 - 100%. The sample tested had the composition given in Table 10.

TABLE 10 : Composition of effluent to ponds at Sutherlands Tannery (liquor filtered through kieselguhr)

Conductivity mS/cm	5,26 mS/cm
Sodium	1 120 mg/l
Calcium	64,5 mg/l
Chloride	1 077 mg/l
Sulphate	92 mg/l
Total carbon	760 mg/l

b) General Hide Corporation, Harrismith

Hyperfiltration of the chrome wash effluent was examined using UOP PA300 and DDS HR98 membranes at 6 MPa. Due to the high electrolyte content of the effluent (40 g/l) only 45% water recovery could be obtained before fluxes became too low to warrant further concentration. (15 l/m2h for UOP membrane and 7 l/m2h for the HR 98 membrane). The composition of the chrome wash effluent is given in Table 11.

TABLE 11 : Composition of chrome-wash effluent
(liquor filtered through kieselguhr)

pH	4,1
Conductivity mS/cm	39,8
Total dissolved solids	40 740
Total carbon	790
Sodium	10 860
Chromium	1 590
Calcium	690
Chloride	9 660
Sulphate	13 900

(All concentrations in mg/l)

c) Silverton Tannery

During batch concentration using the same conditions as in (b) above, 69% water recovery was achieved with fluxes dropping sharply at the initial stages, then more slowly to between 10 - 13 l/m^{2}h.

Analysis of the liquor tested is given in Table 12.

TABLE 12 : Composition of effluent after the SILFLO unit - Silverton

pH	7,4
Conductivity mS/cm	9,16
Total dissolved solids	7 180
Organic solubles	1 980
Inorganic solubles	5 200
Sulphate	2 760
Sodium	1 520
Chloride	1 590
Calcium	360
Total organic carbon	280

In general, problems with fouling are likely to occur, but development of pretreatment methods for the effluent and cleaning procedures for the membranes should be examined for each type of effluent from tanneries. The rejection of inorganic and organic constituents is good. Water recovery however, will depend on the initial salt concentration and very high concentrations will restrict the application of reverse osmosis.

4.1.4.7 Cross-flow microfiltration : use on tannery effluents as a pretreatment process

Samples of effluent streams from various tanneries were selected to determine the effectiveness of cross-flow microfiltration as a pretreatment process before applying reverse osmosis.

In some cases ferric chloride had been used as flocculant. The effluents in general have a very low redox potential

(Eh = -130 mV). Ferric chloride addition will increase the potential at the expense of the added ferric ions, some of which will be reduced to ferrous iron, which will be soluble at the relatively low pH of the effluent. Clearly then, a ferric hydroxide membrane laid down on a cross-flow filter hose would be reduced at a rate depending on the redox potential of the effluent flowing over the membrane. With reduction, the membrane would tend to dissolve.

Ferric chloride is unsatisfactory as a coagulant with the highly reducing effluents, both as a medium for membrane formation, and as a coagulant in clariflocculation settling. In the former case, the membrane will be converted rapidly to the soluble ferrous form. In the latter case, excess ferric chloride must be used to obtain a floc, and a significant proportion of the ferric salt is converted to ferrous iron which thus appears in the clarified effluent.

If reverse osmosis of the clarified effluent is to be attempted, the presence of iron will be troublesome.

a) General Hide Corporation, Harrismith

Effluents arising from the effluent scheme as suggested in pilot studies were selected. (See Section 4.1.4.2 and Appendix 2).

A] Supernatant liquor from pre-lime soak 1 plus pre-chrome effluents 5, 6, 7 and 8.

----- sample (1)

B] + C] supernatant liquor from 2 and 3, plus 10 before ferric chloride addition, i.e. supernatant from lime, lime wash and chrome wash effluents.

----- sample (2)

The composition of these effluents is given in Table 13.

TABLE 13 : Analysis of samples

	Sample 1	Sample 2
pH	7,2	7,8
Conductivity mS/cm	4,74	18,73
TDS	6 028	16 412
Organic solubles	3 554	13 964
Ash	2 474	2 448
Chlorides	1 067	3 159
Sodium	760	4 332
Calcium	24	-
Sulphide $S^=$	13	5,5
Sulphate	121	5 360
Fe	1,5	0,9
Free and saline NH_3	242	970
Protein (Folin)	1 950	3 900
Above analyses on filtered samples		
Total solids	6 464	17 725
Suspended solids	469	2 522
Potential Eh mV 20°C	23,4	-135,3
Isoelectric pH	4,5	-

All concentrations in mg/l.

Sample (1) is representative of 60% of effluent from this tannery as shown in Table 14.

TABLE 14

Operation	Number	Volume of effluent involved kl/d
Lime Section		
Soak	1	33,0
De-hair		
Liming	2	17,6
Wash	3	33,0
Fleshing	4	
Chrome Section		
First wash	5	20,9
Second wash	6	20,9
Delime		
including bate	7	13,1
Wash	8	20,9
Pickle, chrome		
tan & basify	9	-
Wash	10	20,9
		180,3

"Soaks" effluent is made up from combining streams 1, 5, 6, 7 and 8, and has a total volume of 108,8 kl/day.

Cross-flow filtration tests were carried out using a) an aluminium hydroxide film on the medium and b) a diatomaceous earth film on the medium. The run with the aluminium hydroxide layer was conducted with effluent adjusted to an initial pH of 5,5 and in the case of diatomaceous earth the pH was lowered to pH 5.

Both films gave clear permeates. Some TOC rejection occurred in both cases. Fluxes between 15 - 30 l/m^2h were obtained in extended runs.

Sample 2 was treated through a cross-flow microfilter using a hose which had been pretreated to form an aluminium hydroxide film on the medium.

The results of this test are given in Tables 15 and 16.

TABLE 15 : Results from run on sample 2 effluent
(600 ppm Al, pH 5,5)

	Pressure in (kPa)	Pressure out (kPa)	Permeate flux (l/m2h)	Reject flow (l/m)	Velocity (m/s)
Total Recycle	120	100	57 - 43 (over 18h)	8,5	1,3
Batch Concentration	120	100	43 - 16 (over 13h)	8,5	1,3

Analyses of feed and permeate samples during total recycle and batch concentration runs showed some rejection of total carbon and protein. No suspended matter was present in the permeate. The composition of the feed and permeate is given in Table 16.

TABLE 16 : Composition of feed and permeate in cross-flow microfiltration using aluminium hydroxide on nylon hose - Sample No. 2

Analysis	Initial feed for recycle *1	Permeate during recycle	Feed to batch concentration *2	Permeate during batch concentration *2
pH	6,0	6,0	5,4	5,3
Conductivity mS/cm	18,2	18,5	16,6	18,6
Chloride	3 766	3 697	3 820	3 846
Sodium	4 350	3 630	-	-
Iron	9,1	2,2	-	-
Sulphate	5 040	5 360	-	-
Protein	2 035	1 342	2 068	1 452
Aluminium	ND	ND	-	-
TOC	1 244	1 046	1 313	955

Concentrations in mg/l

*1 pH increased from 5,5 during run and HCl was added

*2 sample at 28,5% concentration

ND not detected.

When the preformed layer on the hose was replaced by a diatomaceous earth layer good clarity was obtained and again some rejection of TOC and protein was observed.

The process as a treatment method for removal of suspended solids and as a pretreatment method for feed to a hyperfiltration process, appears to have considerable potential.

b) Effluents from :

i) SA Bata Co Ltd Uitenhage, Cape,
ii) Hanni & Sons Pty Ltd, Nigel, Transvaal,
and iii) Silverton Tannery Co Ltd, Silverton, Transvaal.

The above effluents are end of line effluents after SILFLO treatment. They were all satisfactorily clarified by treatment through a cross-flow microfilter using an aluminium hydroxide or a diatomaceous earth layer. (Orbin, Jan 1985).

Analyses of these effluents are given in Table 17.

TABLE 17 : Analysis of effluents

Analysis	Method	S.A. Bata Co Ltd	Hanni & Sons Pty Ltd	Silverton Tannery Co Ltd
pH		7,6	5,0	7,9
Conductivity (mS/cm)		26,2	28,7	16,1
TDS (*)		17,6	19,5	10,2
Organic solubles (*)		2,4	2,4	1,4
Ash (*)		15,2	17,1	8,8
Chloride	potentiometric	6 753	7 072	2 960
Sodium	atomic absorption	5 128	5 712	2 861
Protein (Folin)	spectrophotometric	1 712	1 012	432
TOC	gaseous oxidation	-	465	409
IC		-	3	71
TC		1 028	468	480

All concentrations (except *) in mg/l.

* concentration in g/l.

TDS - total dissolved solids.

TOC - total organic carbon.

IC - inorganic carbon.

TC - total carbon.

Of the three effluents tested, only effluent (ii), which contained a considerable amount of suspended floc, could be clarified without a preformed layer. No significant rejection of dissolved constituents was obtained in any of the tests on the three effluents. Fluxes through the diatomaceous layer tended to steady out at 10 l/m2h for a circulation velocity of 1,7 m/s.

4.1.4.8 Hyperfiltration tests on permeates from cross-flow microfiltration of tannery effluents

a) General Hide Corporation - Harrismith

The effluent derived from the liming, lime wash and chrome wash operations - sample (2) Section 4.1.4.7a after cross-flow microfiltration was subjected to hyperfiltration. At a water recovery of 35%, the flux was about 15 l/m2h and the rejection of the TC, chloride and chromium good. A precipitate formed during the experiment.

Hyperfiltration of the 'soaks' effluent - sample (1) Section 4.1.4.7a after microfiltration was straight forward. At 70% water recovery, fluxes were high at about 30 l/m2h and rejection of total carbon, chloride and sodium was high. (Simpson, Sept 1984).

b) Effluents after SILFLO treatment followed by cross-flow microfiltration (4.1.4.7(b))

(i) Bata Tannery

Flux decreased steadily throughout both total recycle and batch concentration tests, however, at 62% overall water recovery the flux was 16 l/m2h. Fouling was evident and this may have been due to a precipitate which formed during concentration. (Simpson, Jan 1985).

(ii) Hanni and Sons Tannery

Flux decreased throughout both recycle and batch concentration tests. At 50% water recovery in the first batch concentration cycle the flux dropped to 16 l/m^2h. (Evaporation was not taken into account). A precipitate formed during further recycle/batch mode operation tests and fouling is likely to be a problem.

(iii) At about 40% water recovery, after operation in recycle and batch modes, the flux was about 22 l/m^2h. (Evaporation was not taken into account). Again, a precipitate formed during further recycle/batch mode operation tests and fouling is likely to be a problem.

Rejection of components was reasonable in tests (i), (ii) and (iii) but further tests are necessary before firm recommendations can be made. DDS HR98 membranes were used in the hyperfiltration tests a, bi, bii and biii.

4.1.4.9 Electrodialysis

Electrodialysis of tannery effluents was not conducted. Since in many of the effluents, the organic constituents will include amino acids, separation of organics from inorganics will be poor. Further, the fouling aspects will be determined by the molecular size of the organic fraction and this will vary from effluent to effluent. (Neytzell-de Wilde, January 1985).

Amino acids are amphoteric electrolytes and naturally the mobilities change according to the pH value when the dissociation condition of these radicals changes.

Besides migration of acidic amino acid towards the anode by

permeation through the anion-exchange membrane, approximately the same amount migrates towards the cathode by passing through the cation-exchange membrane with the pH value near the isoelectric point.

4.1.4.10 Carbon adsorption

On the basis of work carried out in Section 4.1.2.4 no tests were carried out on tannery effluents using activated carbon. Work carried out by Vucenta and La Conde (1982) for the Environmental Protection Agency indicated that powdered activated carbon has limited ability to bond COD, BOD, TOC, THA, chromium and oil and grease in tannery effluents.

CHAPTER FIVE : BASIC COST STRUCTURE OF TREATMENT PROCESSES CONSIDERED

The report emphasises that, within the guidelines presented on applicable treatment technologies, each effluent has its own characteristics and detailed pilot investigations are necessary to produce the design data and an economic evaluation.

Installed capital costs of equipment and operating costs are highly dependent on parameters such as site accessibility, complexity of the effluent, sophistication of operation as well as the basic cost structure of the applicable treatment technology.

Basic costs for the desalting of brackish and sea water by hyperfiltration and electrodialysis are given in Appendix 5 solely as a guide. Their interpretation for the treatment of industrial effluents must be carried out with caution.

CHAPTER SIX : CONCLUSIONS AND RECOMMENDATIONS

6.1 Oxidation of Organic Matter in Industrial Waters Using Ozone

(i) Ozone is a powerful oxidant and oxidation of many organic contaminants is technologically possible.

(ii) Various oxidised products will remain in treated waste waters after ozonation.

(iii) Ozonation of low COD waters to oxidise some of the dissolved organic compounds to less harmful or more easily removable substances and to oxidise or breakdown organic substances to more biodegradable forms for their removal on biologically active carbon is a viable process in water reclamation.

(iv) Because of the low efficiency by which pollutants are oxidised and the high cost of the oxidant, ozonation can be considered only in selected applications.

[In order to produce 1 kg ozone/hour from air, approximately 19 kWh of energy, including preparation of air, are required. At R0,05/kWh, this amounts to R0,95/kg ozone. To this must be added capital charges and costs for maintainance etc.]

(v) It is recommended that ozone oxidation should not be considered for grossly contaminated effluents but that use of this oxidant be restricted to specific applications involving low concentrations of materials readily attacked by ozone.

6.2 Wet Air Oxidation in the Treatment of Industrial Waste Waters

(i) As wet air oxidation is a capital intensive, high pressure, high temperature process, its use should be limited to :

a) low volume effluents,

b) waste waters having more than 20 g/l COD so that the process can operate autogenously,

c) waste waters containing biorefractory or toxic materials,

d) waste waters from which chemical recovery is possible.

(ii) The horizontal, multi-compartmented reactor system appears to have advantages over the tower reactor system and it is recommended that this design be considered when necessary.

6.3 Electrodialysis as a Unit Operation in the Treatment of Industrial Waste Waters

(i) The use of electrodialysis in industrial waste water treatment has not been applied to any extent although the process is recognised as a reliable and economical procedure for the desalination of brackish waters.

(ii) The major problems which limit the application of electrodialysis as a waste water procedure are :

a) the salt concentration of the effluent. At low concentration (500 mg/l), the process becomes uneconomic, at higher concentrations 5 000 - 6 000 mg/l, reverse osmosis becomes more economic and at concentrations greater than 0,5 mol/l the membranes tend to lose their permselectivity.

b) some waste water constituents cause membrane poisoning, fouling and scaling and in this respect

large ionised organic molecules are particularly troublesome.

c) Good separation of organics from inorganics is not necessarily achieved ; the degree of separation depends on the nature of the organic constituent.

(iii) It is recommended that accelerated fouling tests be carried out in a suitable flow-through cell to determine effect of the effluent on membranes before electrodialysis in a stackpack.

(iv) The process can be used effectively for the concentration of weak brine solutions (where fouling is absent) up to about 20 g/l NaCl. Energy usage (d.c.) amounts to approximately 1 kWh/kg salt. It is recommended that this application be followed up where possible.

(v) Electrodialysis cannot be used on effluents such as the sulphite spent liquors from a sulphite pulp mill because of severe fouling and it is recommended that no effort be allocated to such work or to work on variants of the electrodialysis process using inert membranes instead of anion-exchange membranes.

(Recommendations regarding soda pulp bleach liquors and effluent from the preparation of oxidised starch are given later).

6.4 Carbon Adsorption in the Treatment of Industrial Waste Waters

(i) As a complete treatment for the removal of all organics from an effluent, adsorption techniques are not economically feasible. It is recommended that carbon adsorption be considered as a unit operation in the final stages of effluent treatment as a polishing operation.

6.5 Cross-flow Microfiltration

Cross-flow microfiltration using polyester or nylon hose as the base medium is a useful pretreatment process for liquors containing suspended solids and colloids that are normally difficult to separate by conventional filtration techniques.

It is recommended that this simple procedure be applied as necessary.

Modification of the base medium by depositing self rejecting dynamic membranes or a layer of a hydrous oxides of certain metals can improve filtration and result in some degree of rejection of organics. It is recommended that this technique be studied and applied where necessary.

6.6 Membrane Processes in the Treatment of Industrial Waste waters

Electrodialysis, ultrafiltration and cross-flow microfiltration, as separation processes, have been discussed in some detail in this report. Hyperfiltration, as a pressure driven membrane separation operation is also discussed, but is well documented elsewhere as well and conclusions regarding the use of these processes is given below only in relation to the specific industries and specific effluents examined in this respect.

6.6.1 Pulp and Paper Industry

6.6.1.1 Sulphite pulp mill effluents

(a) Ultrafiltration of spent liquor gives high rejection of lignosulphonate. The sugars, mainly xylose, and acetic acid pass into the permeate.

The process presents the possibility of recovering valuable lignosulphonates. In addition xylose is a useful chemical for conversion to other commercial

products.

This work is being followed up by SAICCOR.

(b) It has been shown that self-rejecting membranes are laid down by lignosulphonates and it is recommended that this aspect be examined in greater detail.

(c) Hyperfiltration tests have indicated that the weak wash-pit liquors can be concentrated to the same concentration as the spent liquor with good rejection and at a reasonable flux (above 20 l/m^2h at 55% water recovery ; total solids at 136 g/l). The permeates will contain some acetic acid.

(d) The E-stage liquor from the bleaching stage does not give good separation of organics from inorganics by ultrafiltration. Hyperfiltration of this liquor gives good rejection of total carbon ; but some acetic acid passes into the permeate. Flux of about 15 l/m^2h was obtained on a commercial module at 87% water recovery.

(e) The technical feasibility of the use of hyperfiltration on these effluents (c and d) (and therefore permeates from (a)) has been demonstrated and application should be followed up as necessary.

6.6.1.2 Soda pulp mill - bleaching stage effluents

(a) Ultrafiltration does not give good separation of organics from inorganics.

(b) Hyperfiltration gives good rejection of constituents, but fouling tendencies, particularly in the case of the D_1 + D_2 stages, are indicated. This process is being followed up by SAPPI Ltd.

(c) Electrodialysis leads to easy demineralization but fouling of the anion membrane is likely to occur. Longer term tests are being followed up by SAPPI Ltd.

6.6.2 Effluent from the Manufacture of Oxidised Maize Starch Produced by a Wet Oxidation Method

6.6.2.1 Electrodialysis of this effluent resulted in good demineralization with only a small transport of organics across the anion membranes.

The process of manufacture has now been altered and no effluent is produced. Nevertheless, the tests have shown the possible use of electrodialysis for removal of non-fouling ionic material from an effluent containing essentially non-ionised organics.

It is recommended that the use of electrodialysis be investigated further where effluents of this nature arise e.g. in other sections of maize wet milling plants and in distilleries, wineries, malting processes etc.

6.6.3 Effluents from Tanneries

6.6.3.1 When the system of segregated effluents is in operation at the General Hide Tannery at Harrismith, the use of cross-flow microfiltration followed by reverse osmosis should be considered for the 'soaks' effluent.

6.6.3.2 Consideration should be given to physical methods for the recovery of sulphide from the dehairing effluent.

6.6.3.3 Ultrafiltration of tannery effluents is unlikely to give good separation of organics from inorganics mainly because of the spread of molecular size. Many of the effluents, especially the pond effluents contain highly degraded organics. Each effluent stream needs to be considered separately for the application of ultrafiltration.

6.6.3.4 Cross-flow microfiltration is a technique to which serious consideration should be given for removing suspended solids where necessary and as a pretreatment technique for hyperfiltration.

6.6.3.5 In hyperfiltration, problems with fouling are likely to occur and the treatment schemes need to be developed for each effluent. Rejection of inorganic and organic constituents is good, in general. Water recovery, however, will depend on the initial salt concentration and very high concentrations will restrict the application of hyperfiltration.

6.6.3.6 Curing stores, using salt for curing, produce effluents which are unsuitable for processing by ultrafiltration, hyperfiltration or electrodialysis.

Dissolved air and cross-flow microfiltration techniques, before evaporation by vapour compression should be examined.

REFERENCES

Bertera, R ; Steven, H. and Metcalfe, M.
Development of crossflow microfiltration.
The Chemical Engineer, pp. 10-15, June 1984.

Cooper, A.R. (Ed)
Ultrafiltration membranes and applications.
Polymer Science and Technology, Vol 13, Plenum Press, New York and London, 1980.

Drioli, E.
Progress in industrial realisations of ultrafiltration processes ;
In ; Ultrafiltration membranes and applications.
Ed. A.R. Cooper, Polymer Science and Technology, Vol 13, Plenum Press, New York and London, 1980.

Drioli, E. and Cortese, B.
Ultrafiltration processes for pollution control and chemical reuse in the tannery industry.
Desalination, 34, pp. 131-139, 1980.

Drioli, E. and Molinari, R.
I processi di membrana nella razionalizzazione del ciclo conciario.
Acqua-Aria, 3, pp. 231-236, 1984.

Fane, A.G. and Fell, C.J.D.
Removal and recovery of lime sulphide tannery effluents by ultrafiltration.
University of New South Wales (Australia) School of Chemical Engineering.
Report no. 17, January 1979.

Groves, G.R.
Progress report on RO/UF pilot plant treatment trials on spent sulphite and wash pit liquors from SAICCOR.
Binnie and Partners, October 1984.

Groves, G.R. et al
Microfiltration applications in the treatment of industrial effluents.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, 1985.

Kleper, M.H.
A new approach for treatment of spent tannery liquors.
JALCA, 74, pp. 422-437, 1979.

Le, M.S. and Billingheimer, P.J.
Membranes in downstream processing.
The Chemical Engineer, July/Aug., pp. 48-53, 1985.

Lussi, M. and Neytzell-de Wilde, F.G.
Identification of ellagic acid in sulphite pulp mill waste liquors.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, March 1985.

Lussi, M.
A modified method for lignin determination in effluent from the sulphite pulping process, SAICCOR, Umkomaas. Relative value only.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, November 1984.

Michaelis, A.S.
Fifteen years of ultrafiltration. Problems and future promises of an adolescent technology.
In : Ultrafiltration membranes and applications, A.R. Cooper, Ed.
Polymer Science Technology, Vol 13, Plenum Press, New York and London, 1980.

Neytzell-de Wilde, F.G.
Ultrafiltration tests on effluents from a curing store - Vleissentraal, Cato Ridge.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, 21 February 1984.

Neytzell-de Wilde, F.G.
Research into the treatment of industrial effluents with high salinity and organic content. Progress Report.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, October 1983.

Neytzell-de Wilde, F.G.
Membrane fouling in electrodialysis.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, March 1985.

Neytzell-de Wilde, F.G.
Ultrafiltration of sulphite pulp mill lignosulphonate effluent liquors at different concentrations.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, 21 November 1984.

Neytzell-de Wilde, F.G.
Oxidation of organic matter in effluents using ozone.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, 13 March 1985.

Neytzell-de Wilde, F.G.
Wet air oxidation.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, March 1985.

Neytzell-de Wilde, F.G.
Electrodialysis.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, March 1985.

Neytzell-de Wilde, F.G.
The use of electrodialysis in the recovery of lignosulphonate from sulphite pulp mill effluents.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, March 1985.

Neytzell-de Wilde, F.G.
Preliminary examination of effluents from the bisulphite pulp mill SAICCOR, Umkomaas.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, September/November 1984.

Orbin, A.E.
Preliminary investigation into self-rejecting membrane formed in a cross-flow filtration unit.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, 6 September 1984.

Orbin, A.E.
An investigation into the effect of temperature and pressure on the behaviour of a self-rejecting membrane formed by a dilute wash-pit liquor, SAICCOR pulp mill, Umkomaas.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, 2 October 1984.

Orbin, A.E.
The effect of temperature and concentration on the cross-flow filtration of sulphite pulp mill, Umkomaas.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, 12 February 1985.

Orbin, A.E.
Examination of effluents - General Hide Corporation, Wet-Blue Tannery, Harrismith, OFS.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, July 1984.

Orbin, A.E.
Cross-flow filtration of the combined lime and chrome effluent from General Hide Corporation, Wet-Blue Tannery, Harrismith, OFS.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, August 1984.

Orbin, A.E.
Cross-flow filtration of a composite of pre-lime soak and pre-chrome soak effluents : General Hide Corporation, Wet-Blue Tannery, Harrismith, OFS.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, August 1984.

Orbin, A.E.
Cross-flow filtration of tannery effluents.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, January 1985.

Orbin, A.E.
Cross-flow filtration - Literature review.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, 1985.

Philp, E.
Limiting current density of NaCl.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, March 1984.

Pohland, H.W.
Reverse osmosis : In : Handbook of water purification.
Ed. W. Lorch
McGraw Hill Book Co. (UK) Ltd., 1981.

Simpson, A.
Reverse osmosis of permeates produced by cross-flow microfiltration of effluents from General Hide Corporation, Harrismith, OFS.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, September 1984.

Simpson, A.
Reverse osmosis : SAICCOR E-stage effluent.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, October 1984.

Simpson, A.
Progress Report : Reverse osmosis : SAICCOR E-stage effluent on FilmTec SW30-2514 membrane.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, November 1984.

Simpson, A.
Carbon Adsorption.
Pollution Research Group, Chemcial Engineering Department, University of Natal, Durban, March 1985.

Simpson, A.
Reverse osmosis : Pretreated Bata Tannery effluent.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, January 1985.

Sissou, H.A. ; Kraus, W.G. and Johnson, J.S.
Cross-flow filtration in physical-chemical treatment of municipal sewage effluents.
EPA 600-2-76025, 1976.

Solymosi, A.
Critical current density.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, 1984.

Solymosi, A.
Concentration of sodium chloride using electrodialysis.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, April 1985.

Solymosi, A.
Batch electrodialysis of SAPPI (Enstra) D_1 + D2 effluent.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, 1985.

Solymosi, A.
Electrodialysis of oxidised maize starch effluent.
Pollution Research Group, Chemical Engineering Department, University of Natal, Durban, June 1984.

Sourirajan, S. and Matsuura, T.
The science of reverse osmosis. An essential tool for the Chemical Engineer.
The Chemical Engineer, No. 385, pp. 359-368 ; 376, 1982.

Strathman, H.
Membrane separation processes.
Journal of Membrane Science, 9, pp. 121-181, 1981.

Vucenta, J. and La Conde, K.V.
Powdered activated carbon adsorption isotherms for selected tannery effluents.
EPA 600-S2-82-065, August 1982.

APPENDIX 1

DETAILS OF TANNERY AND FELLMONGERY ESTABLISHMENTS

Name	Location	Type of Tannery	Raw Materials	Water	Usage	Effluent Treatment	Effluent Disposal
Bachs Tannery	Huguenot C.P.	Veg. Tan.	1 000	16	16	Nil.	Municipal sewer.
Coja Tannery*	Vereeniging	Chrome Tan.	15 000	150	10	Aeration and Settling.	Municipal sewer.
Edendale Tannery (Pty) Limited	Edendale Natal	Veg. Tan.	8 000	80	10	Settling Ponds.	Spray irrigation.
Exotan (Pty) Limited	Port Elizabeth C.P.	Chrome Tan. (Exotic skins)	1 800	170	94	Primary Settling. Balancing and Aeration. Coagulation. Sec. Sedimentation.	Municipal sewer.
General Hide Corporation Wet-Blue Tannery Ltd.*	Harrismith O.F.S.	Chrome Tan. (wet-blue)	10 000	150	15	Primary Settling. Aeration and Balancing. Secondary Settling.	Spray irrigation.

APPENDIX 1 (cont. 1)

Name	Location	Type of Tannery	Raw Materials	Water	Usage	Effluent Treatment	Effluent Disposal
Hanni & Sons (Pty) Ltd.*	Nigel, Transvaal	Chrome Tan.	25 000	530	20	Balancing and Aeration. Air Flotation.	Municipal Sewer.
Italpelli	Rustenburg	Game Skins	250	1,5	6	Nil.	Municipal Sewer.
King Tanning Co. Ltd.	King William's Town C.P.	Chrome Tan.	26 000	900	34	Primary Settling.	Land Irrigation.
Klein Karoo	Oudtshoorn	Chrome Tannery (Ostrich skins).	1 200	200	160	Primary Settling.	Evaporation Ponds.
Kwiktan	Krugersdorp	Game Skin	300	15	50	Settling.	Municipal Sewer.
Massop & Son (Pty) Ltd.	Cape Town	Finishing	7 000	360	50	Screening. Holding Tank for pH Adjustment.	Municipal Sewer.
Pelts Products (Pty) Ltd.	Port Elizabeth C.P.	Wet-Blue Plant Fellmongery (Lime-sulphite/enzyme-sweating)	45 600	700	15	Screening. Balancing and Aeration. Oxygenation. Coagulation. Activated Sludge.	Municipal Sewer.

APPENDIX 1 (cont. 11)

Name	Location	Type of Tannery	Raw Materials	Water	Usage	Effluent Treatment	Effluent Disposal
Perseverance Wool Pullery Co.	Perseverance C.P.	Pullery (enzyme-sweating)	14 000	200	14	Nil.	Evaporation Ponds.
S.A. Bata Co. Ltd.	Uitenhage C.P.	Chrome Tan.	20 000	250	12	Balancing and Aeration. Air Flotation.	Evaporation Ponds.
S.A. Cape Fellmongers (Pty) Limited	Port Elizabeth C.P.	Fellmongery (lime sulphide)	4 000	500	125	Balancing and Aeration.	Municipal Sewer.
Silverton Tan. Co. Ltd.	Silverton Pretoria	Chrome Tan. Veg. Tan.	30 000	500	17	Balancing and Aeration. Air Flotation.	Recycle 40 - 60%. Remainder to Municipal Sewer.
Sutherlands Tannery Ltd.*	Pietermaritzburg Natal	Chrome Tan. Veg. Tan.	Wet-Blue 7 500 Wet-Salted 5 500	450	35	Nil.	Evaporation Ponds.
Tannery Protea	Butterworth	Chrome Tan.	8 000	200	25	Settling Ponds.	Municipal Sewer.

APPENDIX 1 (cont. III)

Name	Location	Type of Tannery	Raw Materials	Water	Usage	Effluent Treatment	Effluent Disposal
Thorer Fur (Pty) Limited	Cape Town	Chrome Tan. (Skins)	1 000	120-140	130	Balancing, Settling. Aeration, Settling.	Municipal Sewer.
Transvaal Hide & Skin Producers	Johannesburg Transvaal	Wet-Blue Plant	21 000	150	7	Aeration. Chrome recycle.	Municipal Sewer.
Urbans Inds (Pty) Ltd.	George C.P.	Chrome Tan.	3 300	-	-	Filter through saw-dust.	Soak-away.
Velskin Prods. (Pty) Limited*	Hammanskraal Transvaal	Chrome Tan. (sheepskin)	3 000	80	26	Settling.	Municipal sewer.
Western Tanning Co. Ltd.*	Wellington C.P.	Chrome Tan.	32 000	18	18	Primary Settling. Aeration.	Evaporation Ponds.

NOTE * : This data correct as of June 1985. However these tanneries are in the process of improving their existing effluent treatment systems.

Appendix 2

Brief details of the operations, water and effluent quantities at the General Hide Corporation Wet-Blue Tannery at Harrismith, OFS.

A2.1 Water Usage

The factory operates on a 5 day week and uses 200 kl water per day to treat 1 000 hides per day.

A2.2 Hides

Hides are received from the City Deep (Langlaagte) and Cato Ridge abattoirs. The hides are treated with Busan 72 (fungicide) and need to be processed promptly.

A2.3 Process

A2.3.1 Lime Section

A2.3.1.1 Soak Operation

Hides, 50 at a time, are weighed into a lime drum. 500 hides are charged. Water at 150% of the hide mass is pumped into the drum and Cismollen BH (0,2% of hide mass) is added. (Cismollen BH is a soaking agent). The hides are soaked at 28-30°C and pH 6,9-7 for 6 hours. (During this period the drum is rotated for 20 minutes and then held stationary for 10 minutes).

A2.3.1.2 Liming Operation

After the six hours soaking period, the drum is drained. A fresh charge of water at 28-30°C is pumped in to 80% of the hide mass. 2% lime and 3% sodium sulphide (on hide mass) is then added and the drum run continuously for 90 minutes.

Thereafter, over 780 minutes the drum is run for 20 minutes and stopped for 10 minutes. The pH and temperature conditions are 12-12,5 and 28-30°C.

After the liming operation the drum is drained and water at 150% of the hide mass is pumped in at 28°C. The hides are washed for 35 minutes and the drum is again drained. The hides are then dropped.

Total water to drain is approximately 90-100 kl/day.

A2.3.2 Chrome tanning section

A2.3.2.1 Wash Operation

After liming the hides are machine fleshed and then weighed and transferred to the chrome tanning drum (there is approximately a 10% gain in mass of the hides as a result of the liming process).

The hides are washed twice for 20 minutes each time with water at 80% of the wet hide mass. The temperature of washing is 35°C. The water is discharged to drain.

A2.3.2.2 Delime Operation

The drum is charged with 50% water at 35°C, 1,75% ammonium sulphate, 0,01% manganese sulphate and 0,4% Triton X-114. The drum is run for 40 minutes. The pH target value is between 8,9 to 9,2.

A2.3.2.3 Bate Operation

0,4% bate (enzyme) is added to the drum and the drum rotated for a further 30 minutes (fat is removed in this operation). The drum is then drained and the hides washed with 80% water at 25°C for a further 20 minutes. The liquid is then run to drain.

A2.3.2.4 Pickle Operation

Salt*, 2% (of hide mass) and 0,88% calcium formate are added to the drum and the drum run for 10 minutes. Recycle liquor (50%) from following stage is pumped into the drum and the drum run for 25 minutes. The contents are then acidified with 1,25% of sulphuric acid and the drum run for a further 60 minutes at pH 2,9-3,3.

*without a recycle system 6% NaCl would be added. The NaCl is added to avoid swelling of the hide.

A2.3.2.5 Chrome Tanning Operation

The required quantity of chrome (8% required) is then added and the drum run for 15 minutes. A chrome test is carried out. 0,05% Busan 72 is then added and the drum run for 120 minutes at 27°C.

A2.3.2.6 Basify Operation

After the 120 minutes under the above conditions the pH is increased by adding 0,67% soda ash. (This fixes the chrome). 0,125% Rexyntan AL3 is pumped in over a period of 2 hours. The drum is then run for 570 minutes, at pH between 3,3-3,6 and temperature about 34°C. If the liquor is below pH 3,3 soda ash is added to a max. pH of 3,6. A chrome test is carried out.

After 570 minutes of the above operation the drum is drained into a collecting pit.

Water 80% at 35°C is then pumped into the drum with 0,02% Triton X-114 and the drum run for 30 minutes. The drum is drained to effluent and the hides dropped.

The hides are then 'dried' to 50% moisture by passing through

a mangle, and packed (polythene wrap) for despatch.

Total water to drain for the tanning section is approximately 90-100 kl/day.

A2.4. Control

The liming and tanning operations are shown in the Lime Yard Control Ticket and Chrome Tanning Ticket.

From these it will be seen that the quantities of water and effluent in the various stages can be calculated - values are shown in brackets in the remarks column of the tickets. (1 000 hides before chrome stage : say 22 000 kg and after liming say 26 100 kg).

LIME YARD CONTROL TICKET

FOLIO NO.:.....HIDE SOURCE:.....DATE IN:.....DATE OUT:.....

WEIGHT:.....NO. OF HIDES:.....DRUM NO.:.....

Operation Stage	Qty	Process Description	Run Time	Testing	Start	Stop	Remarks
SOAKING [1]		Add Hides (Pump in Water) 150% Water @ 28°C					[33 kl per 1000 hides]
		Add 0,2% Cismollan BH Run Drum for	6 hr (Run 20') (Stop 10')	 Temp: pH:			Req.) Temp:) 28 -30) pH 6.9-7
DRAIN			20'				
LIMING [De-hair 2]		(Pump in Water 80% Water @ 28°C Add 2% Lime Add 3% Sod. Sulphide Run Drum continuously Check Float Run drum for	 90' 780' (Run 20') (Stop 10')	 Temp: pH:			[17,6 kl per 1000 hides] Req.) Temp:) 28-30) pH: 12 - 12
DRAIN		(Pump in water) Add 150% Water @ 28°C	20'				[33 kl per 1000 hides]
WASH [3]			35'				
DRAIN			20'				
DROP							
MECHANICAL FLESHING [4]							

GENERAL HIDE CORPORATION
CHROME TANNING TICKET

FOLIO NUMBER:.....NO. OF HIDES:.....DATE IN:.....DATE OUT:.....

WEIGHT:.....DRUM NO.:.....CYCLE NO.:.....

Operation Stage	Qty	Process Description	Run Time	Testing	Start	Stop	Remarks
1. WASH [5]		(Pump in Water) 80% Water @ 35°C	20'				[20,9 kl per 1000 hides]
DRAIN			20'				
WASH [6]		(Pump in Water) 80% Water @ 35°C	20'				[20,9 kl per 1000 hides]
DRAIN			20'				
2. DELIME [7]		(Pump in Water) 50% Water @ 35°C 1,75% Amm. Sulphate 0,01% Man. Sulphate 0,4% Triton X-114	40'	Pene: pH:			[13,1 kl per 1000 hides])) Req pH)
3. BATE		0,4% Bate	30'	pH:			) 8.9-9.2
4. DRAIN			20'				
WASH [8]		(Pump in Water) 80% Water @ 25°C	20'	Pene:			[20,9kl/d per 1000 hides]
DRAIN			40'				

Chrome Tanning Ticket (Continued):

Operation Stage	Qty	Process Description	Run Time	Testing	Start	Stop	Remarks
5. PICKLE		ADD (To Drum)					
		.....% Salt					
		.....% Calcium Form					
		then run for	10'	SG:			
	[9]	(Pump in 50% Recycle Liq)	25'				
		Acidified with 1,25% Sulp. Acid		Pene:			)
		Run Drum for	60'	pH: Temp.			) Req pH) 2.9-3.3
6. CHR. TAN		.....% Chrome	15'	Chr. Test (A)			
		0,05% Busan 72	120'	Temp:			
7. BASIFY		0,67% Soda Ash					
		0,125% Rexyntan AL3					
		Pump in over 2 hours					
		then run drum for:	570'	pH:			) Req pH
		If below 3.3 add Soda		Chrome Test (B)			) 3.3-3.6
		Ash until max pH 3.6		Temp:			
				Boil Test			
8. DRAIN		Into Collecting Pit	30'				[20,0 kl
		(Pump in Water)					per 1000
	[10]	80% Water @ 35°C					hides]
		0,02% Triton X-114	30'				
		Drop					

Appendix 3 Sutherlands Tannery, Ltd, Pleisislaer, Natal, 1983

A3.1 Water usage

The factory operates on a 5 day week and uses 240 m^3 water from the Umsindusi river, 5 m^3 municipal water and approximately 12 m^3 borehole water (total 257 m^3d^{-1}). The factory has a permit to use 800 m^3d^{-1}. Effluent discharge from the works into the evaporation pond systems is estimated at about 240 m^3d^{-1}.

A3.2 Hides

The hides received into the factory are :-

(i) blue-wet hides for further processing.
(ii) chemically treated hides for vegetable tanning and further processing.

The tannery treats 700 hides per day ; 5,5 tons to vegetable tanning and 7,7 tons to the chrome yard for processing.

A3.3 Process

A3.3.1 Vegetable Tanning

The hides are soaked overnight in water containing calcium hypochlorite (approximately 1 kg $Ca(OCl)_2$ per 4 m^3 water).

After soaking the hides are washed in rotating drums to remove salt. The next stage involves soaking the hides for one week in pits filled with an aqueous solution containing the following chemicals :-

0,8% Na_2S, 3% $Ca(OH)_2$ and 0,2% NaOH

The discharge from this section is about 20 - 25 m^3d^{-1}.

The hides are then passed through unhairing and fleshing machines before being steeped overnight in the pickling pits. The pits contain sodium-hexametaphosphate (5° Be') at pH 2,2, (H_2SO_4). There is no effluent discharge from this operation.

After pickling, the hides are transferred to the last of a series of vegetable tanning pits. The vegetable tanning pits at the head of the series contain wattle extract at 120°C and the concentration decreases to approximately 30°B in the last pits where the freshly pickled hides enter. The hides travel up the series over a period of three weeks. At the end of this period the hides are bleached in two bleach pits containing sodium metabisulphite.

Effluent from the tanning pits is only about 3 m^3d^{-1} siphoned off from the last (weakest) pit.

In order to achieve a higher degree of tannage and better filling, the hides are then treated in a rotating drum with chemicals such as lignosulphonic acid, fat, urea, magnesium sulphate, naphthalene sulphonic acid, oxalic acid, dimethylformamide, sugar. There is no effluent from this treatment operation, in the case of sole hides. Harness hides, however, are washed and the effluent is of the order of 12 m^3d^{-1}.

The hides are air dried (slightly above ambient) for one week to about 20% moisture. Any dry material on the surface after this period is removed by dry drumming in the presence of a small amount of bleaching oil.

The hides are then treated with 40% sulphonated fish oil and 60% mineral oil and allowed to dry again for 7 - 10 days in an air stream.

Thereafter the hides are subjected to finishing operations such as light and heavy rolling to smooth out the surfaces.

These hides are used for soles, harnesses etc.

A3.3.2 Wet-blue hides

After splitting and levelling the hides are subject to further treatment with chrome, other tanning agents, dyeing and fat addition.

The effluent from this section amounts to about 120 - 150 m^3 and is not separated from the effluent from the vegetable tanning section.

A3.3.3 General

This is an old tannery which no longer produces wet-blue hides because of the effluent requirements.

Nevertheless the effluent from the processing of wet-blue hides amounts to over half of the total plant effluent.

The effluent from the vegetable tanning section is combined with that from the wet-blue processing section and is allowed to flow to a series of evaporation dams. Effluent from the last dam is sprayed onto grassland.

There is no deliberate discharge into the Umsindusi river although under high flow conditions a pond may be discharged.

Appendix 4 Vleissentraal Koop Bpk. Slagpale Curing Store - Cato Ridge 1983

A4.1 Introduction

Hides and skins are received from the neighbouring abattoir (SA Abattoir Corp) and are treated the same day.

A4.1.1 Hides

Hides (800/day) are fleshed by hand and then treated with biocides in tumblers. The hides are transferred to tanneries as soon as possible after treatment. The small amount of effluent from this operation, 1 600 kl/m (including domestic effluent for 140 people at 100 l/d) is passed on to the large biological treatment plant which handles the total abattoir effluent and the acceptable effluent from the satelite industrial section of Cato Ridge.

A4.1.2 Skins

Skins (5 000/day) are sorted into three main types, viz., those for

a) wool and skin recovery
b) skin recovery and
c) wool recovery with some conversion of the skin to 'chamois' type leather.

Skins have to be cured because there are many grades, which are used in different processes and therefore need to be stored.

On some skins, type (c) above, metabisulphite can be used. The metabisulphite is sprayed onto the defleshed skin and the treated skin is then dried at 35°C. The number of skins treated this way is small say 800 -1 000/day in winter period. Salt curing would be used for these skins if there were no

effluent problems. Most of the skins, after hand defleshing are lightly sprayed with metabisulphite and then covered with Grade 1 coarse salt. These skins are restored in piles and the fluid allowed to drain for 48 hours. Approximately 0,75 - 0,85 litres per skin is drained. When the skins are 'dry' the excess salt is brushed off and the skins are then ready for transfer to tanneries. Approximately 120 tons of clean salt is used per month. Half this quantity is retained on the skins.

A4.1.3 Effluent from the skins

The effluent collected from the treatment area is flocculated using aluminium sulphate and lime (chlorine is used as a biocide) in three flocculators. The clear liquor is used to wash salt, from which 50% is recovered as crystal salt. The effluent from this operation is then transferred to a receiving/blending pond and then to an evaporating pond. Evaporation rates, however, are unsatisfactory at the site and an improved effluent treatment scheme is planned.

The brine from the floor drainage will be treated in a SILFLO unit. Clear brine from this unit will be used to wash used salt and clean brine will be evaporated using vapour compression to recover salt for the curing process. The various operations are illustrated in Figures 1 - 5.

The effluent from the treatment of hides is free from salt and this effluent is at present blended with the biological treatment plant. It is proposed however, that this effluent will also be treated by the SILFLO process to reduce the high COD load about 18 000 mg/l, to more acceptable levels (2 000 mg/l) for biological treatment.

FIGURE 1 : Diagram of effluent flows

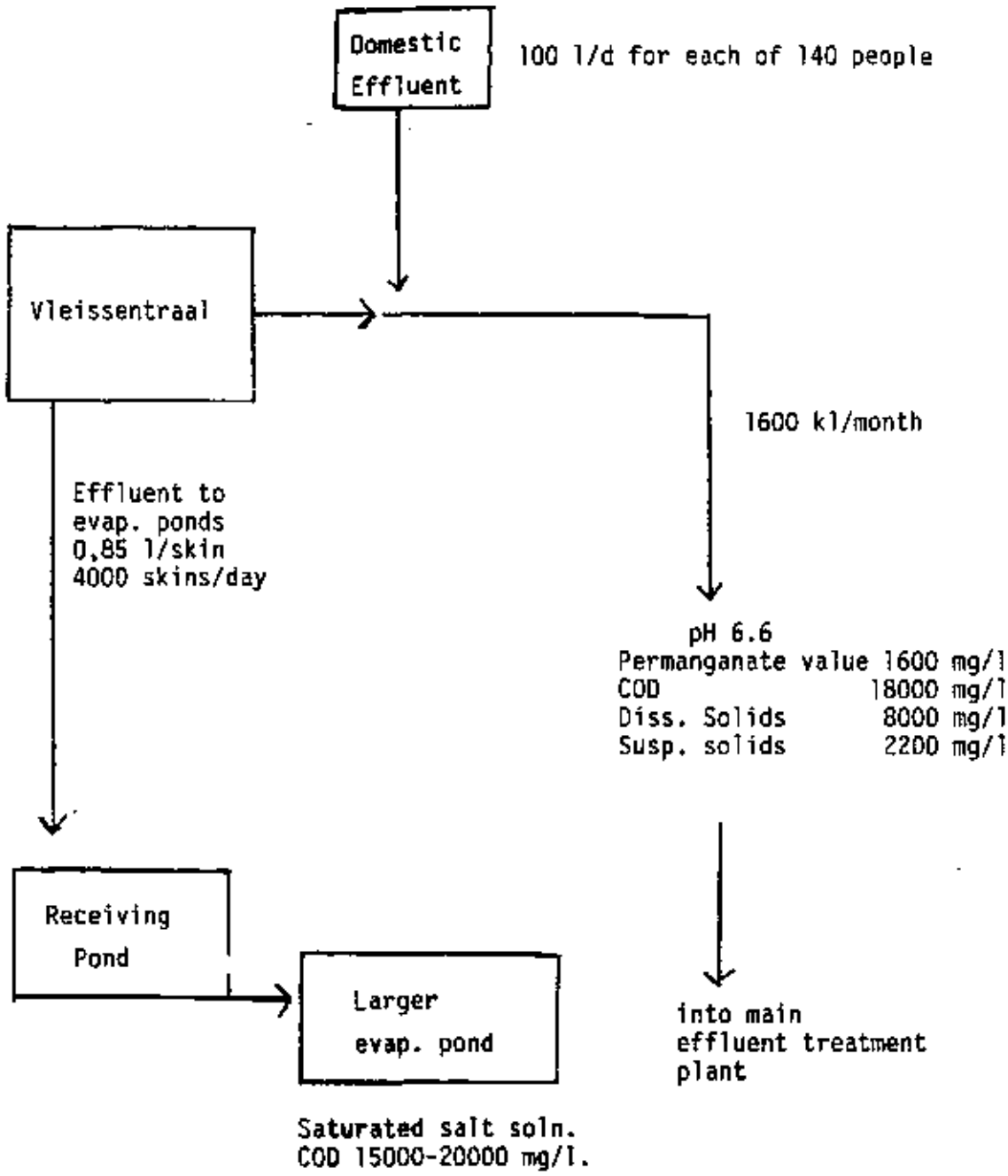


FIGURE 2 : Flow scheme for salt curing process for skins

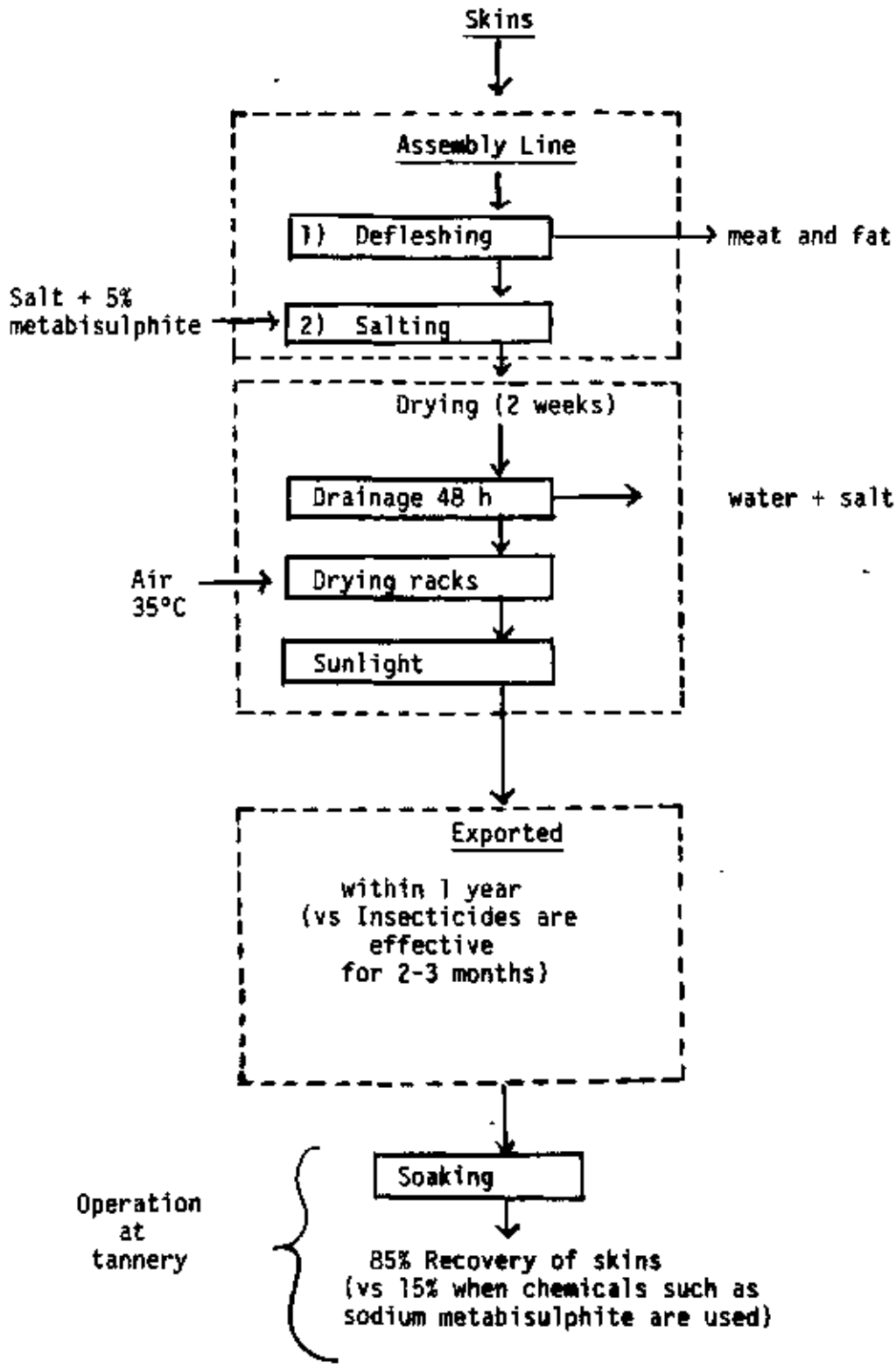
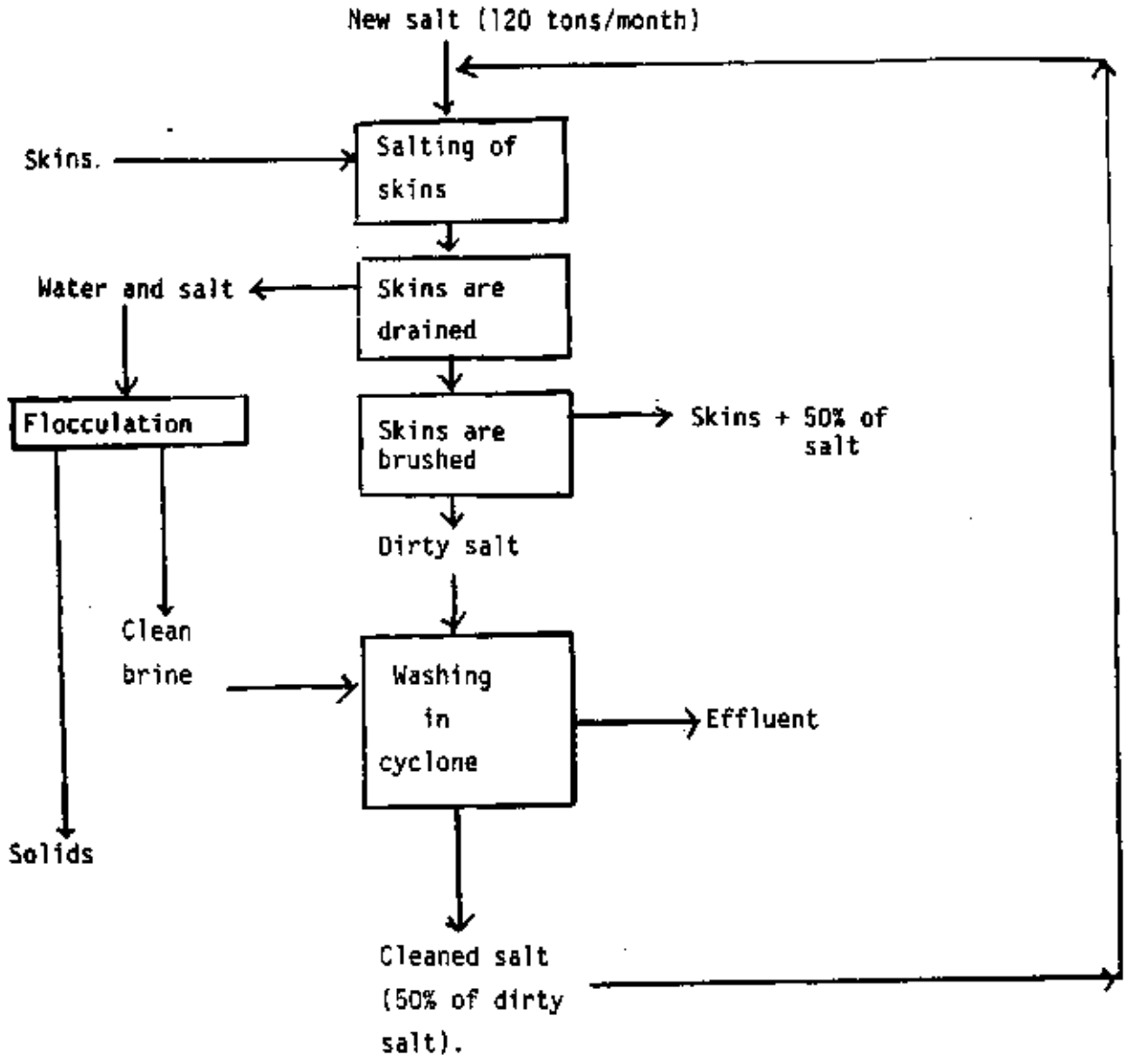


FIGURE 3 : Flow scheme for salt



NOTE : The salt has to be washed to help prevent "red heat".

FIGURE 4 : Water recovery system from salt curing process

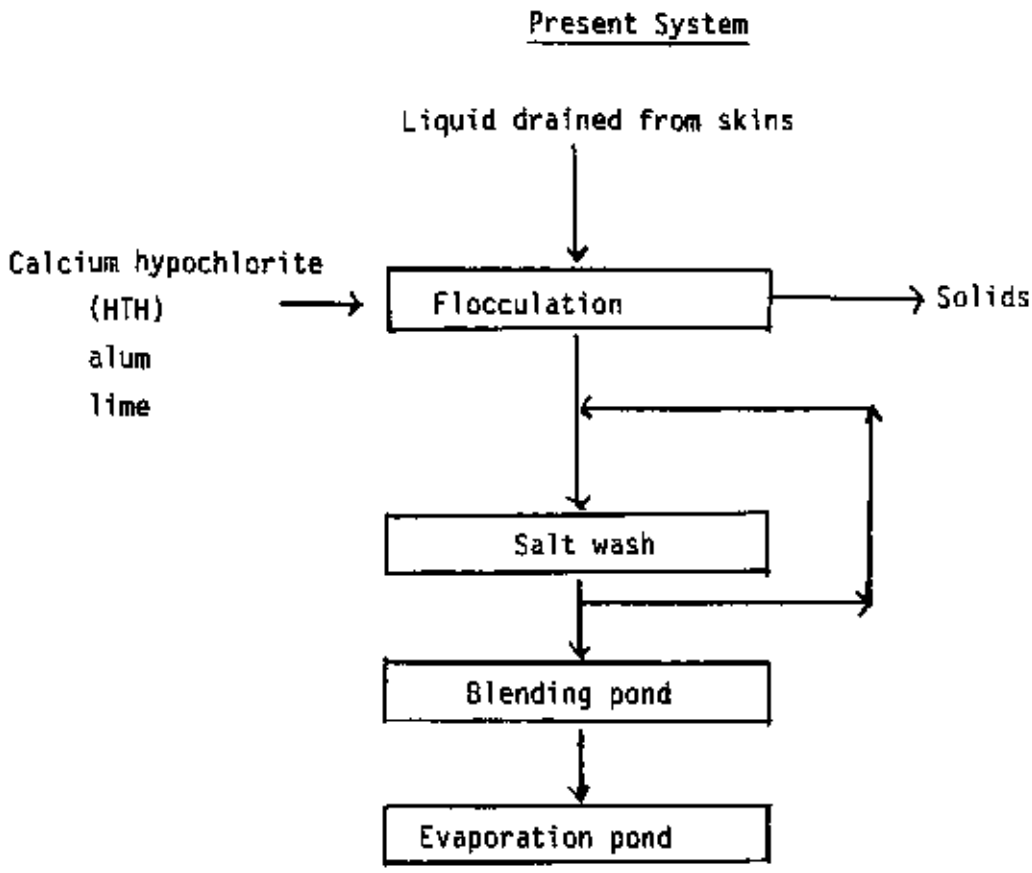
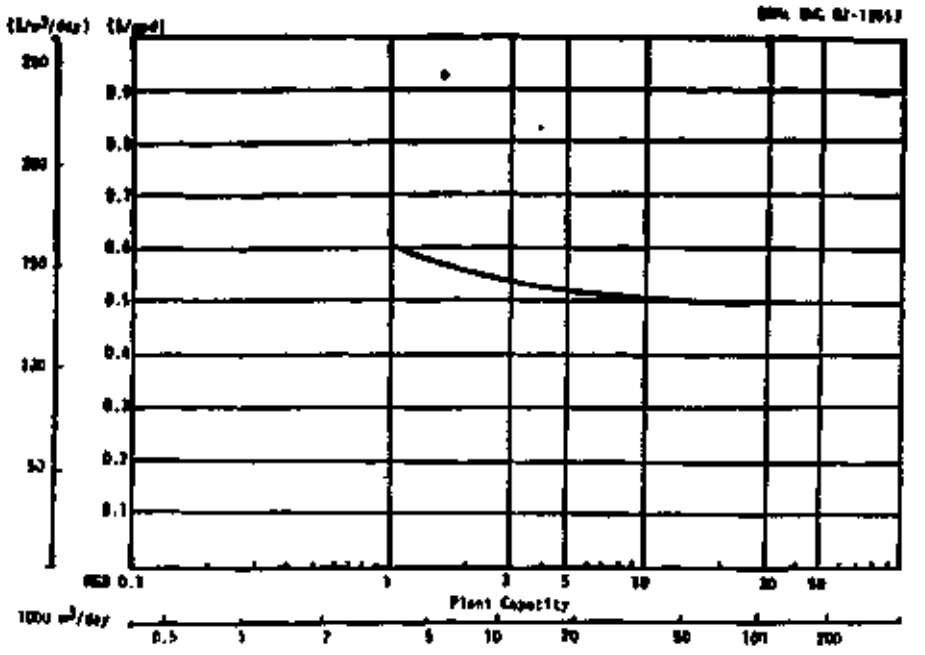


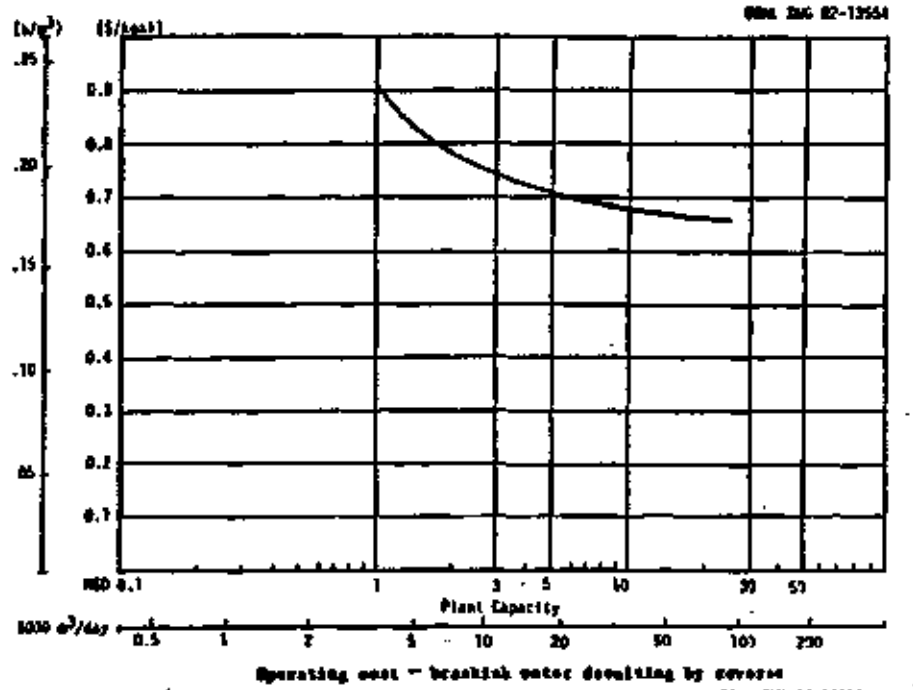
FIGURE A5.1

a)



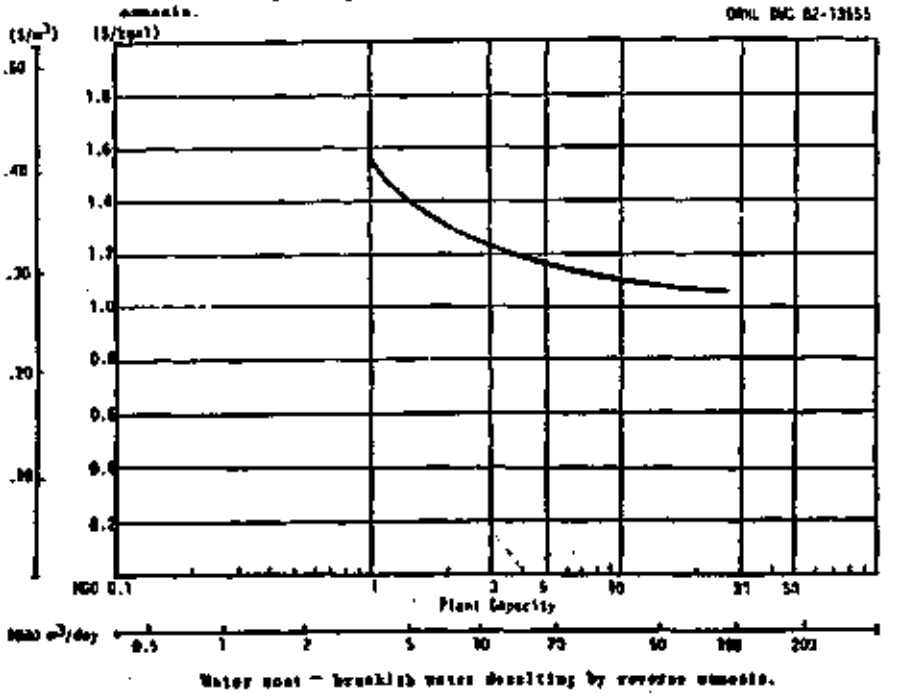
Capital equipment cost – brackish water desalting by reverse osmosis.

b)



Operating cost – brackish water desalting by reverse osmosis.

c)



Water cost – brackish water desalting by reverse osmosis.

a)

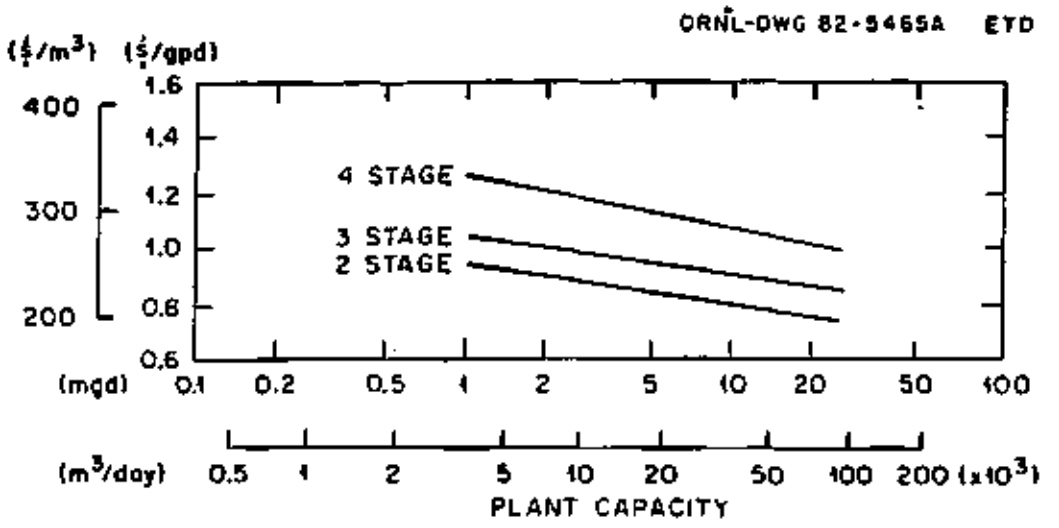
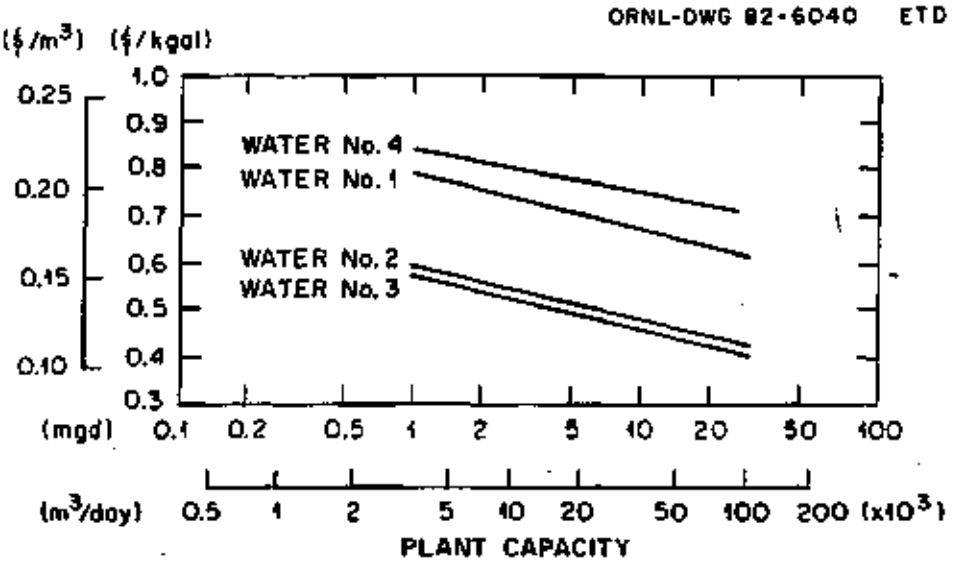


FIGURE A5.2

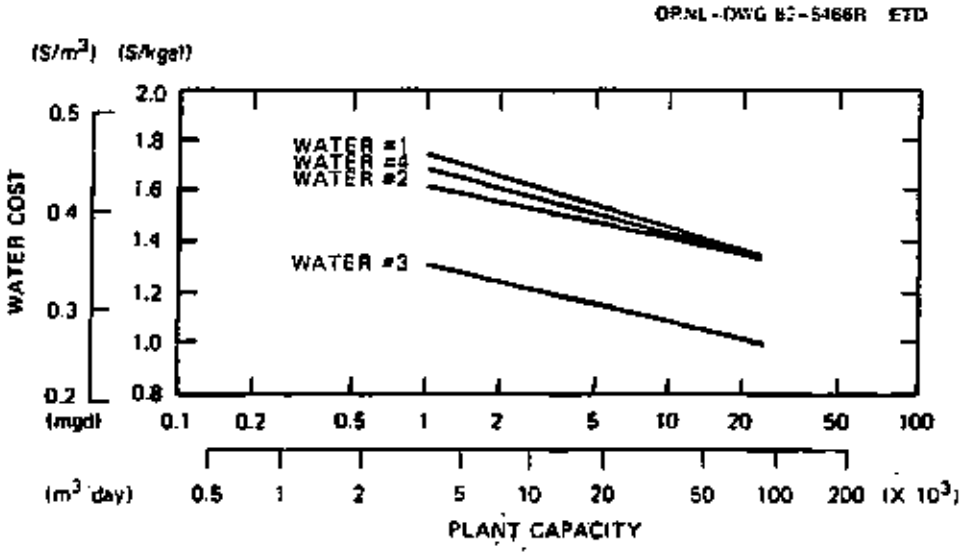
CAPITAL COST - BRACKISH WATER DESALTING BY ELECTRODIALYSIS

b)



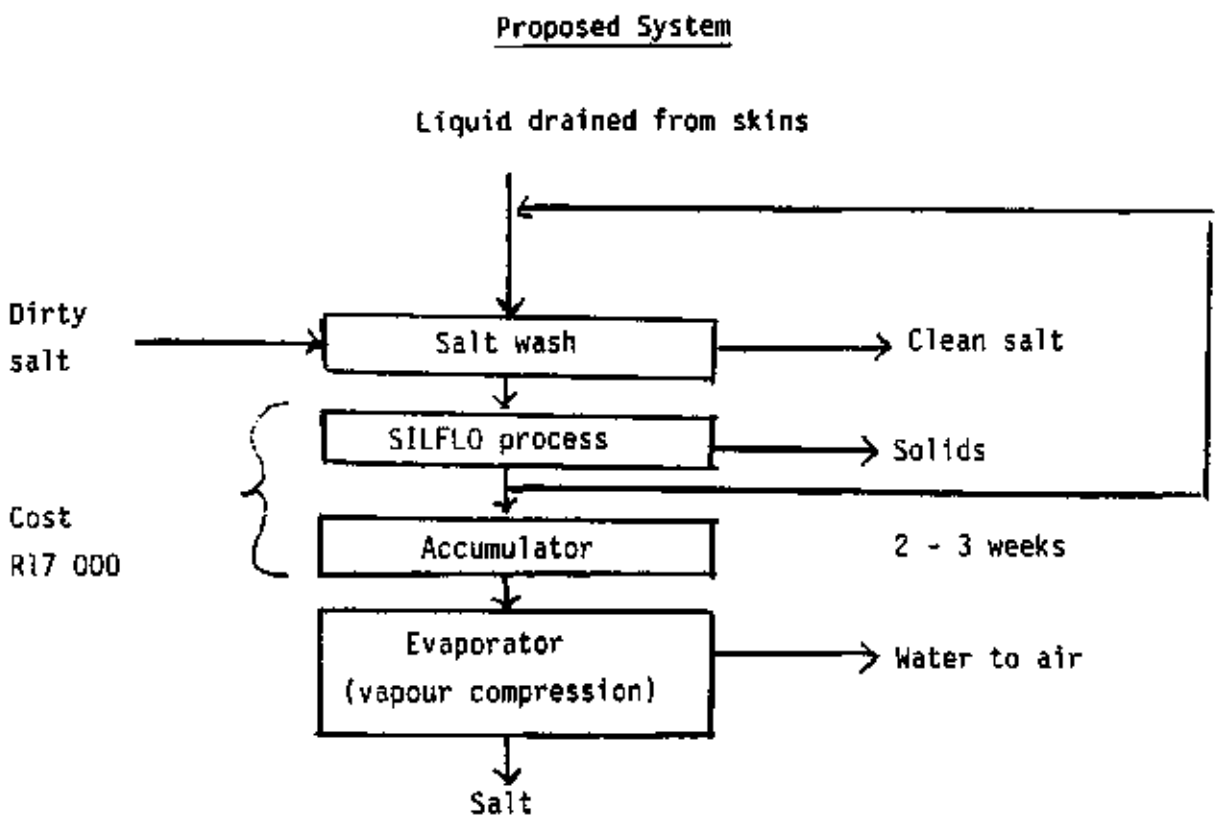
Operating cost — brackish water desalting by electrodialysis.

c)



Water cost — brackish water desalting by electrodialysis.

FIGURE 5 : Water recovery system from salt curing process



APPENDIX 5 Basic Cost Structure of Some Advanced Treatment Technologies

A5.1 Brackish Water Desalination by Hyperfiltration (Reverse Osmosis) and Electrodialysis

Detailed information is given in the following references :

(i) Reed S.A. 'Desalting Seawaters and Brackish Waters - 1981 Cost Update'. ORNL/TM8191, 1982.
(ii) Applegate L.E. 'Membrane Separation Processes'. Chemical Engineering, June 11, 1984.

Figure A5.1 gives basic capital equipment costs, operating costs and water costs for reverse osmosis of brackish water ; similarly, Figure A5.2 for electrodialysis.

A5.2 Seawater Desalination by Hyperfiltration

Basic capital equipment costs, operating costs and water costs for reverse osmosis of seawater are given in Figure A5.3.

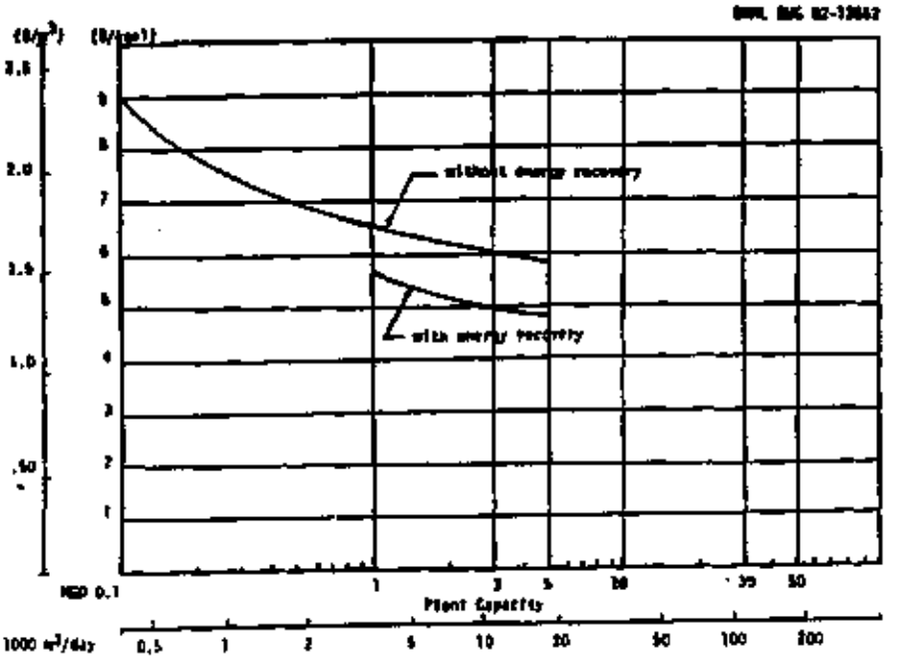
A5.3 Tubular or Plate/Frame Ultrafiltration and Hyperfiltration

Skid mounted units of this type (of relatively small size) often fall into the basic capital cost range of R1 500 - 2 500/m^2 of membrane area.

A5.4 Tubular Fabric Cross-Flow Microfiltration

Skid mounted units of this type fall into the basic capital cost range of R70 - 200 m^2 of membrane area.

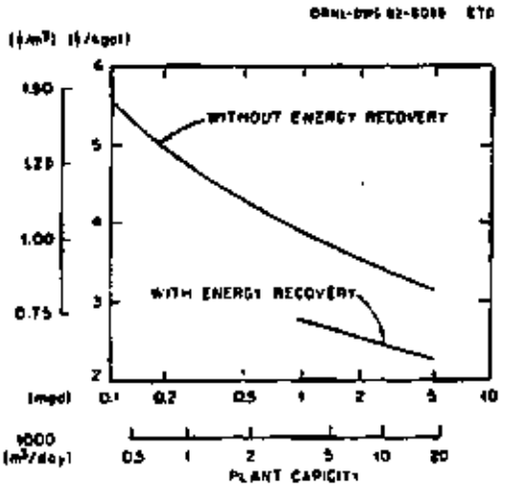
a)



Water cost = seawater desalting by reverse osmosis.

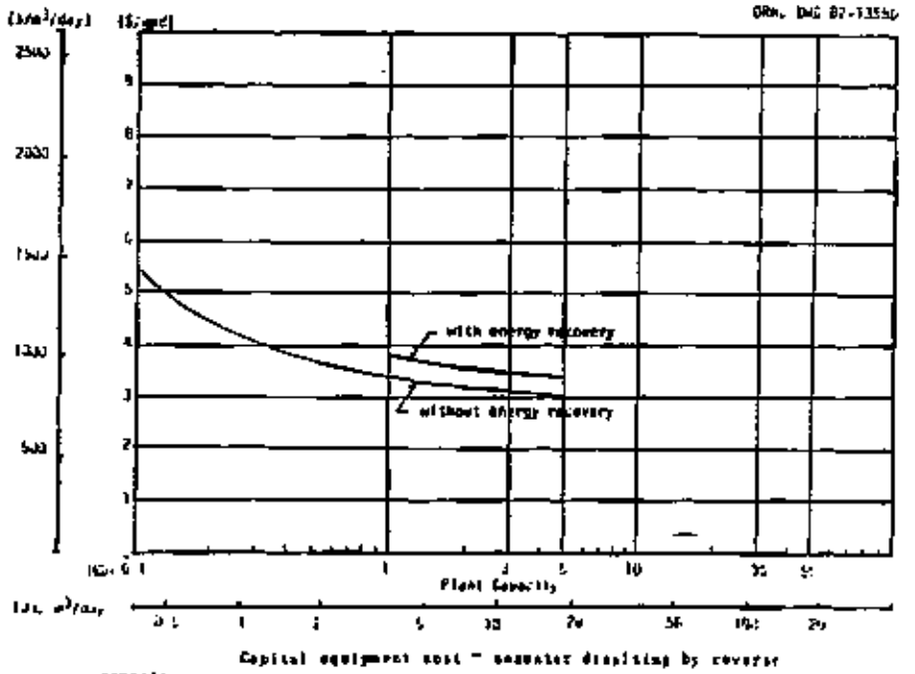
FIGURE A5.3

b)



Operating costs = seawater desalting by reverse osmosis.

c)



Capital equipment cost = seawater desalting by reverse osmosis.