WATER RESEARCH COMMISSION PROJECT NO. 188

AN INVESTIGATION INTO WATER AND EFFLUENT MANAGEMENT IN THE PULP AND PAPER INDUSTRY : TECHNICAL PERFORMANCE EVALUATION OF THE PILOT PLANT TREATMENT OF PULP BLEACH EFFLUENTS BY CROSS-FLOW MICROFILTRATION AND REVERSE OSMOSIS

FINAL REPORT

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EXECUTIVE SUMMARY

Industrial effluents with high salinity and organic contents, if discharged directly, will seriously affect the quality of the water environment, especially at the local level. One such effluent is that generated during the bleaching stage of pulp and paper manufacturing. South African pulp mills have low water usages compared to international standards. This is attained by extensive internal reuse and recycling of process streams. However, acid bleach streams, because of their high chloride content, typically 1 to 2 g/ℓ, are unsuitable for reuse within the mill.

In 1981 SAPPI Ltd. contracted with the Pollution Research Group to investigate the development of a treatment system for the acid bleach effluents from their pulp mills at Enstra and Ngodwana which discharge 5 000 m^3/d and 7 000 m^3/day of this effluent respectively. The application of advanced wastewater treatment technology was considered necessary to control these effluents as water recoveries greater than 90 % were required. Successful application would result in the pulp mills approaching a zero discharge state.

Two technologies were chosen for evaluation:- dynamically formed reverse osmosis membranes and conventional reverse osmosis membranes.

Dynamic membranes theoretically offered several advantages over conventional membranes, including high flux rates, minimal membrane regeneration costs, and no pretreatment or temperature limitations. During 1982, studies were undertaken into the formation and performance of dynamic membranes. Hydrous zirconium oxide membranes or dual layer membranes:- zirconium oxide base layer with organic polymer overlay, were formed on stainless steel support tubes. A range of membranes with differing salt rejections and permeate fluxes were produced. Unfortunately the required specifications with respect to overall salt rejection and permeate flux could not be met. Furthermore, on exposure to the bleach effluent the membrane flux and salt rejection characteristics decreased, indicating that acid bleach effluent was not amenable to treatment by dynamically formed reverse osmosis membranes. Therefore, during 1983, research into the suitability of the effluent for treatment by conventional reverse osmosis membranes was undertaken.

Bench scale tests indicated that a two-stage pretreatment sequence of lime flocculation and cross-flow microfiltration followed by sodium carbonate addition and further cross-flow microfiltration was capable of producing a filtrate of suitable quality for feed to the reverse osmosis membranes.

During the second half of 1984 a reverse osmosis pilot plant capable of handling a continuous flow of 4,2 m^3/h of pretreated bleach effluent was designed, manufactured and installed at the pulp mill at Enstra. The plant was commissioned and handed over to SAPPI in February 1985. The hire of the pilot plant was funded by the Water Research Commission in terms of a contract entitled *An Investigation into Water and Effluent Management in the Pulp and Paper Industry : Technical Performance Evaluation of the Pilot Plant Treatment of Pulp Bleach Effluents by Cross-flow Microfiltration and Reverse Osmosis.*

Almost immediately problems with the cross-flow microfiltration (CFMF) unit arose. These problems had not been envisaged during design nor indicated by laboratory bench tests. These problems limited the amount of feed produced for the reverse osmosis unit to such an extent that in October 1985 the CFMF unit was redesigned. In January 1986 a tube cleaning assembly was installed after which the CFMF unit functioned with specifications.

Concurrent with problems leading to poor performance from the CFMF unit, the bleach effluent was found to contain free chlorine. Chlorine is a major restriction in the use of many reverse osmosis membranes as it degrades the membrane. Chlorine was not indicated in laboratory analysis of the effluent at the University of Natal, and tests by SAPPI laboratories showed that after 2 to 3 days of standing (a time period less than effluent transport time to Durban) the effluent was free of residual chlorine. Furthermore, the chlorine concentration of the effluent was variable and fluctuated at random intervals. A chlorine stripping column was installed in August 1985.

The combination of these unforeseen problems led to under utilisation of the reverse osmosis unit for much of 1985. When sufficient pretreated effluent with no residual chlorine became available and was fed to the reverse osmosis plant it became apparent from specific flux data that membrane fouling was occurring. The possibility of membrane fouling had been recognized during laboratory bench scale experiments. The foulant encountered in these tests was thought to be either calcium sulphate or calcium carbonate, both of which could be controlled in the reverse osmosis environment by chemical dosing of the feed and implementation of a planned cleaning programme. However, the severity of the fouling was unexpected and necessitated further laboratory tests using a simulated pilot plant sequence. The foulant was examined by X-Ray diffraction and shown to be calcium oxalate. The solubility of calcium oxalate is 7 mg/ℓ.

An additional pretreatment step to removed excess calcium from the effluent with sodium carbonate was implemented, and a second CFMF unit was installed at the plant in April 1986, ensuring that feed for the RO unit had reduced calcium concentrations, thus preventing the formation of calcium oxalate. Subsequently the reverse osmosis unit functioned satisfactorily with significant improvement and maintenance of the specified permeate flux and with only weekly chemical cleaning of the membranes. The product water produced by the reverse osmosis unit at 75 % water recovery was of specified quality and suitable for reuse within the mill circuit.

The research contract terminated in June 1986. Although beset by problems, the data obtained from laboratory bench-scale tests and operation of the pilot plant, demonstrates that the proposed treatment sequence for acid bleach effluent is capable of producing product water of a quality suitable for reuse within the mill circuit. Thus, together with reduced water consumption, reduced effluent discharge load, and the possibility of chemical recovery from the concentrated brine, the treatment offers a route towards the full closure of the pulp mill and a zero discharge status. A total of 10 publications and 13 conference papers have used information gathered during the course of this project.

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1 INTRODUCTION

The discharge of industrial effluents into the water environment unless adequately purified, 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 system is, however, not always available. The main types of industrial effluents which cause problems on discharge in this regard are those that contain :-

(i) significant quantities of non-biodegradable organics,

(ii) toxic or potentially toxic compounds,

(iii) significant quantities of mineral salts, acids or bases,

(iv) 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 conservation of water sources.

(ii) Improvement management of toxic materials, biologically intractable organic materials and mineral salts.

(iii) Increased industrial recycling of water and reuse of treated effluents.

(iv) The recovery of chemical pollutants and their reuse.

With the steadily increasing cost of water and disposal charges of effluent along with the future tightening up 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 is limited. However, the application of advanced wastewater treatment technology for the control of these effluents is technically feasible using combinations of the following processes : membrane separation, adsorption, thermal separation and chemical oxidation.

1.1 Bleach Effluent from the Pulp and Paper Industry

The pulp and paper industry has several problems associated with the treatment and discharge of their effluents. One of the major concerns is the high load of dissolved salts and poor biodegradability of the bleaching effluents.

New pulp mills, such as the SAPPI Ngodwana mill, are designed with a very low water usage ; 5 to 10 m^3/ton of pulp as against conventional mill water usage of 40 to 100 m^3/ton. This is attained by extensive internal reuse and recycling of process streams. Conventional bleaching has a chloride load of 130 to 200 kg/ton of pulp but incorporation of an oxygen bleaching stage reduces this to about 30 kg/ton. This permits recycling and cascading of certain wastewaters within the bleaching process and to the pulping circuit. The pulping liquors are treated by an evaporation - chemical recovery boiler system in which the organic fraction is burnt and the inorganic fraction is reconstituted for use as process chemicals. The alkaline extraction bleach wastewaters are reused within the process and do not constitute a discharge problem. However, because of the tight water budget the acid bleach streams are very concentrated and are unsuitable, because of the high chloride content, for addition to the thermal recovery system.

The acid bleach wastewaters typically contain up to 5 g/ℓ of total solids. The major constituents being 1 to 2 g/ℓ of chloride and 0,3 to 0,8 g/ℓ of total organic carbon. It has a low pH (2 to 4) and a temperature of 50 to 60 °C. The new Ngodwana pulp mill will discharge up to 7 000 m^3/d of this effluent while the Enstra mill discharges 5 000 m^3/day.

The development of a treatment system for the acid bleach effluents provide the key to full closure of the pulp mill. Already South African pulp mills have very low water usages compared to the international standard and the incorporation of the proposed treatment system will allow pulp mills to approach zero discharge or comply with the General Discharge Standards.

Table 1 shows a typical analysis of the acid bleach effluent at the Enstra and Ngodwana mills.

Arising out of a detailed test work programme sponsored by SAPPI, a treatment process has been developed to remove both the inorganic and organic pollutants at high water recoveries from the acid bleach effluents in the pulp industry. The product water is of a suitable quality for reuse in the pulp mill.

In order to confirm the bench scale results and to provide the necessary design information, an on-site technical performance evaluation of the treatment process was necessary.

This final report summarises the results of the initial membrane process screening tests, bench scale tests and the design and operation of a 80 kℓ/day pilot plant.

TABLE 1 TYPICAL ANALYSIS OF ACID BLEACH EFFLUENT		
Determinant	Ngodwana	Enstra
pH	1,94	2,95
Conductivity	1 769	398
Total Solids	-	4 080
Total Organic Carbon	800	415
Calcium	86	53
Magnesium	511	271
Sodium	510	320
Chloride	2 110	1 173
Temperature	-	35 - 45
All units in mg/ℓ except for pH, temperature (°C) and conductivity (mS/m)		

2 OVERVIEW OF BLEACH EFFLUENT TREATMENT

2.1 Introduction

The ideal solution for the treatment of the bleach effluent would be :-

(i) water recovery for recycle,

(ii) chemical recovery for reuse or sale.

Three treatment steps would be required to implement the above solution. These steps are represented in Figure 1.

The following processes either individually or in combination can be used to solve steps 1, 2 and 3 in the above diagram.

(i) Reverse osmosis.

(ii) Ultrafiltration.

(iii) Nanofiltration.

(iv) Cross-flow microfiltration.

(v) Ion-exchange.

(vi) Electrodialysis.

(vii) Evaporation.

(viii) Electrolysis.

(ix) Incineration.

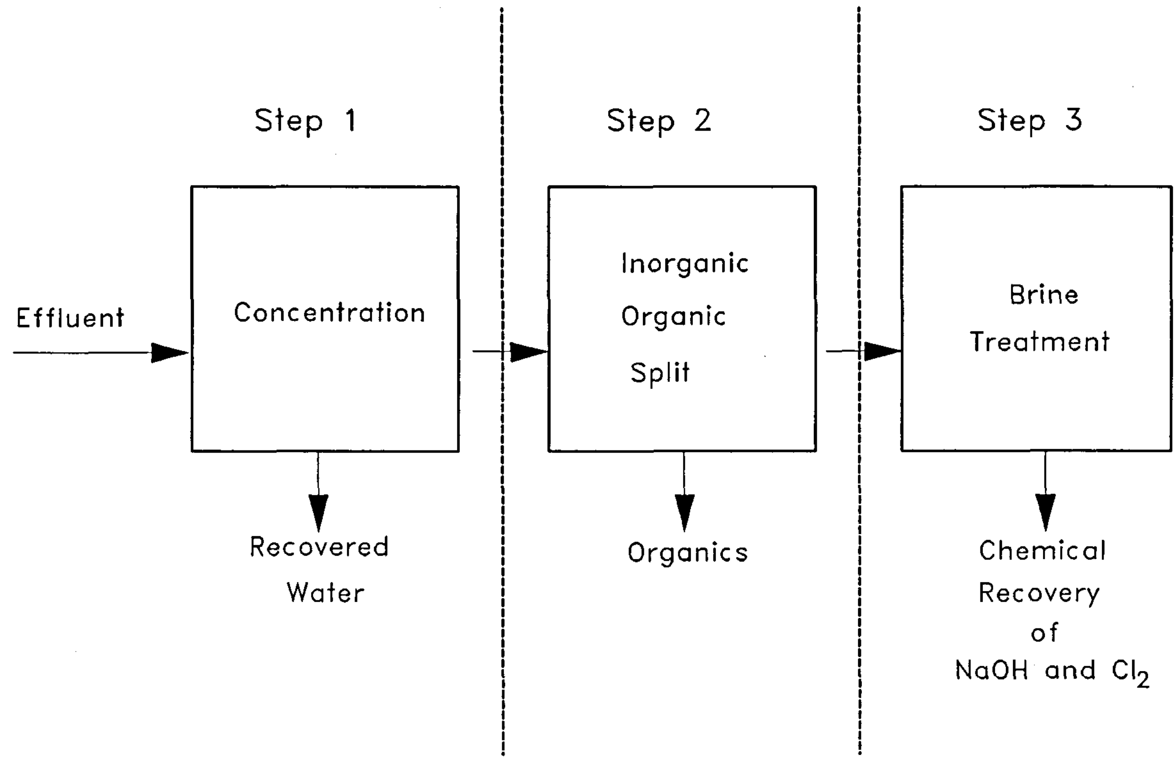

FIGURE 1
BLEACH EFFLUENT - IDEAL SOLUTION

A preliminary cost exercise was done by SAPPI to evaluate the various options and process routes (Appendices A1.1, A1.2, A1.3 and A1.4).

A research programme was initiated in 1981 by SAPPI at the University of Natal, Durban, to investigate reverse osmosis as a means towards solving the bleach effluent problem.

The research programme objectives and personnel from 1981 to 1986 are presented in Appendix A2.

Two types of membrane technologies were considered suitable and required evaluation. They were :-

(i) dynamically formed reverse osmosis membranes,

(ii) conventional reverse osmosis membranes.

Initially the dynamic membrane option was thought to be the most suitable of the two membrane systems because of the following advantages :-

(i) high flux rate resulting in reduced membrane area,

ii) easily regenerated membrane at minimal costs,

(iii) indefinite support life - sintered stainless tubes,

(iv) no pretreatment of bleach effluent is required,

(v) no temperature or chemical limitations.

2.2 Membrane Separation Theory

The overall water quality obtained from a reverse osmosis (RO) system is dependent on the membrane point rejection and the percent water recovery of the system.

Percent water recovery :-

$$(WR) = \frac{Volume\ of\ product}{Volume\ of\ feed} \times 100$$

Membrane point rejection percentage σ:-

$$\sigma = \frac{C_f - C_p}{C_f} \times 100$$

Composite permeate concentration, $\bar{C}_p$:-

$$\bar{C}_p = \frac{1 - (1 - WR)^{(1-\sigma)}}{WR} \times C_{Fo}$$

Water quality :-

$$\beta = \frac{\bar{C}_P}{C_{Fo}}$$

Where C_f = concentration of species in feed at time (t)
C_p = concentration of species in permeate at time (t)
C_{Fo} = concentration of species in initial feed

The relationship between water quality, water recovery and membrane point rejection is shown in Figure 2.

From Figure 2 it is clear that if a particular water quality in the permeate is required then a significantly larger water recovery is obtained from a higher rejection membrane. In addition the volume of the concentrate is significantly decreased even though it will have an increased concentration.

2.3 Concentrate Treatment

The reject stream from the RO system contains high concentrations of organics and inorganics. The disposal of the effluent is a problem and treatment using nanofiltration membranes and chlor/alkali technology was envisaged as a possible treatment route.

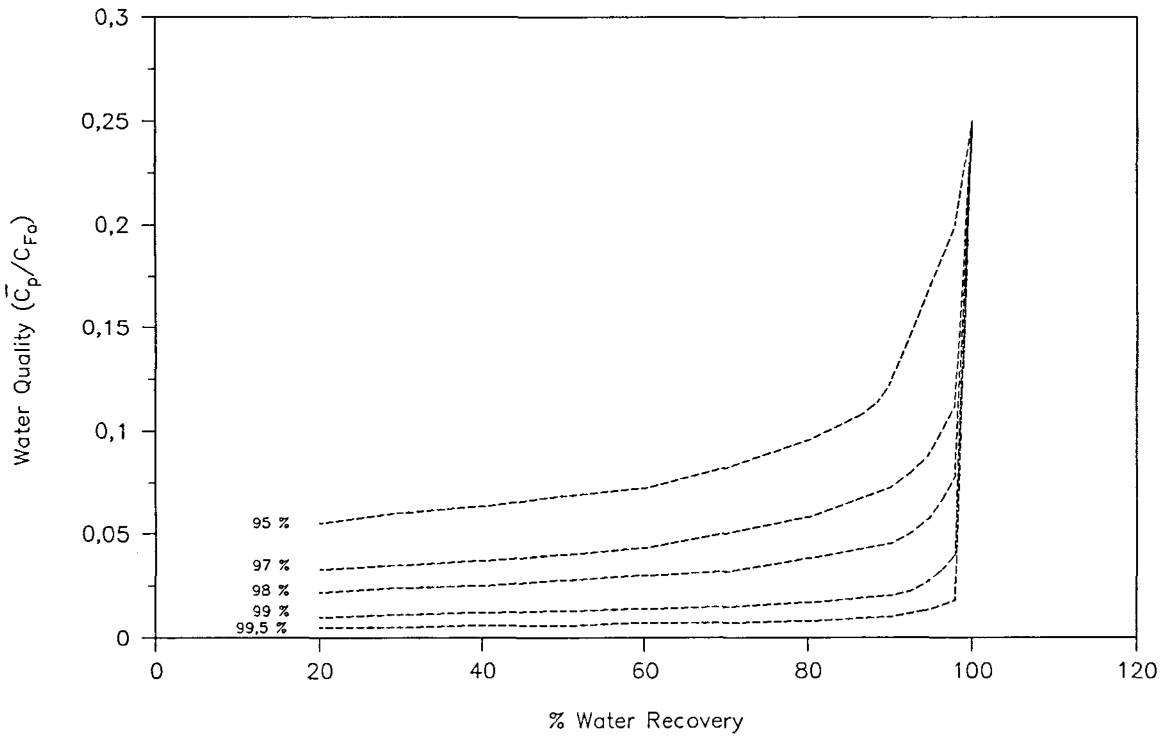

FIGURE 2
WATER QUALITY AS A FUNCTION OF PERCENTAGE WATER RECOVERY

Nanofiltration membranes will split the brine into an organic and an inorganic fraction. The organic fraction would be further concentrated and finally incinerated. The inorganic, high chloride, fraction would be processed in electrolysis cells for recovery of chlorine and caustic soda.

The flow diagram envisaged for brine treatment is depicted below in Figure 3.

When considering any treatment option the overall solution must entail a brine or concentrate treatment stage as shown in Figure 1. In order to make this stage of treatment as small and inexpensive as possible the volume of brine or concentrate to be treated must be kept to a minimum. It is therefore desirable to obtain as high a percentage water recovery as possible during the initial concentration stage.

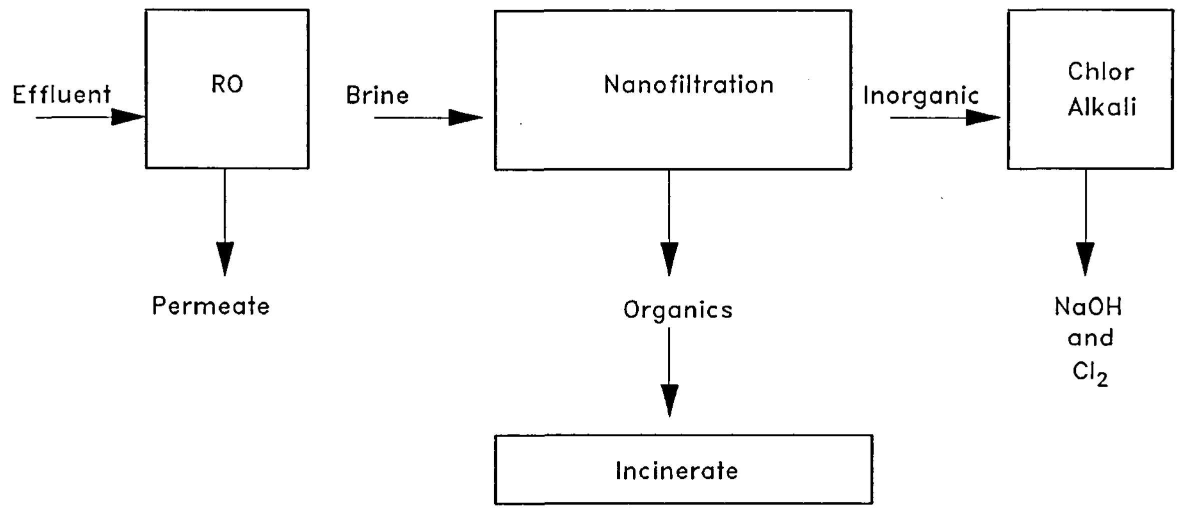

FIGURE 3
PROPOSED BRINE TREATMENT

3 BENCH SCALE : BLEACH EFFLUENT TREATMENT

3.1 Dynamic Reverse Osmosis Membranes

Dynamic membranes are formed *in situ* by passing a solution containing a polymeric metal hydroxide (e.g. hydrous zirconium oxide) through a fixed porous tube under high pressure (Appendix A3). It is possible to chemically remove and reform the membrane on the porous support tube.

The research programme objectives were to investigate dynamic membrane formation, membrane fouling and membrane/feed interaction.

The initial aim was to develop a dynamic membrane with the following properties :-

(i) 90 % overall chloride rejection (water quality ß = 0,1) at 85 % water recovery (i.e. a point rejection of 95 %).

(ii) High flux (75 to 100 ℓ/m²h; minimum flux 50 ℓ/m²h).

(iii) Stable (physically and chemically).

(iv) Easily formed.

(v) Anti-fouling or easily cleaned.

The high rejection dynamic membrane required for treatment of effluent of this nature is usually of the dual layer type i.e. hydrous zirconium oxide base layer with an organic polymer overlay.

Various membraning techniques were employed to produce the hydrous zirconium oxide base layer. It was possible to produce a spectrum of membranes with differing salt rejections and permeate fluxes (Appendix A4.1).

The characteristics of the best zirconium base membranes were as follows :-

Point salt rejection (%)	7	8	11	14	30
Flux (ℓ/m^2h)	694	358	761	274	126

The target base membrane to be used for dual layer formation was a hydrous zirconium oxide with a salt rejection of 10 to 20 % at 500 ℓ/m^2h.

Dual layer membranes were produced using two organic polymers (polyacrylic acid (PAA) and polyvinyl alcohol (PVA)) of varying molecular weight on a hydrous zirconium oxide base layer.

The characteristics of the best dual layer membranes were as follows :-

Point salt rejection (%)	72	47	47
Flux (ℓ/m^2h)	80	87	128

The membranes resulting from this second stage of formation when exposed to the effluent gave fluxes of 15 to 80 ℓ/m^2h with point salt rejections of between 70 to 85 % (Appendix A4).

Point salt rejection (%)	72	74	81	82
Flux (ℓ/m^2h)	80	50	15	35

These permeate fluxes were half of those that were considered in the preliminary cost exercise done by SAPPI (Appendix A1).

On exposure to the effluent the dual layer dynamic membrane flux and salt rejection characteristics decreased. Colour rejections were normally excellent and 90 to 95 % colour removal based on ADMI (American Dyestuff Manufacturers' Institute) values were consistently achieved (Appendix A4.3).

A literature survey was undertaken to obtain a better understanding of the chemistry involved in dynamic membrane formation (Appendix A3).

No further improvement in the flux - rejection characteristics of dynamic membranes were achieved. The research programme emphasis was then switched from dynamic to conventional membrane technology.

3.2 Conventional Reverse Osmosis Membranes

Conventional membranes are manufactured by laying down a membrane material on a porous substrate. Conventional membranes are fixed membranes and cannot be removed or reformed. This type of membrane is commercially available from a number of suppliers.

Each membrane has different characteristics as regards rejection and chemical compatibility (Appendix A6). Preliminary investigations on a flat sheet laboratory scale rig using conventional reverse osmosis membranes (DDS) showed marked fouling when run against untreated bleach effluent. Chemical cleaning of the membranes using the manufacturer's suggested chemicals did not restore the membrane fluxes, this indicated that irreversible fouling of the membranes had taken place. Lime neutralised effluent showed a marked decrease in the rate of fouling of the membranes (Appendix A5.1 and A5.2).

Three 4 inch diameter spiral wrap reverse osmosis elements (FilmTec, UOP and Du Pont) were evaluated during the course of the bench scale investigation to determine the most suitable membrane for the bleach effluent application.

3.3 PRETREATMENT

Various treatment methods to remove the fouling constituents form the effluent prior to reverse osmosis were examined. These were :-

(i) Ultrafiltration using conventional membranes.

(ii) Ultrafiltration using dynamic membranes.

(iii) Flocculation.

3.3.1 Ultrafiltration Using Conventional Membranes

Ultrafiltration of the effluent using a conventional Abcor HFK element gave a reduction of 25 to 30 % of the total soluble organic carbon (TOC) in the effluent. Ultrafiltration fluxes were low (20 to 25 ℓ/m^2h) at the original feed concentration. Effluent pretreated using ultrafiltration when run against the reverse osmosis membranes gave flux and reject results similar to those obtained with lime pretreated effluent (Appendix A5.2).

3.3.2 Ultrafiltration Using Dynamic Membranes

Hydrous zirconium oxide dynamic ultrafiltration membranes underwent a severe flux decline when exposed to the effluent. Conductivity rejections between 18 to 24 %

and TOC rejections between 50 to 60 % were recorded (Appendix A5.3). Capital costs associated with low fluxes (50 to 120 ℓ/m^{2}h) precluded this pretreatment option from further investigation.

3.3.3 Lime Flocculation

Flocculation of the effluent using lime showed that, at pH values of 10,5 to 11,0, up to 30 % of the TOC and 99 % of the magnesium was removed (Appendix A5.4). Removal of magnesium was considered advantageous as it would reduce the alkali earth metal loading of the brine solution that would be processed for chemical recovery.

3.4 Bench Scale Reverse Osmosis of Pretreated Bleach Effluent

Bench scale reverse osmosis tests using 4 inch diameter spiral wrap reverse osmosis elements (FilmTec FT30 and UOP PA300) showed that there was a marked decrease in the fouling nature of effluent treated with lime (Appendix A5.5). Using the FilmTec element, specific flux decreased from 35 ℓ/m^{2}h.MPa to 20 ℓ/m^{2}h.MPa during the test period, indicating that the membranes had fouled. Chemical cleaning was able to restore the membrane flux to its original value. The UOP element rejection declined irreversibly during the experimental run.

Calcium concentrations in the effluent after lime treatment were increased from 50 to 80 mg/ℓ. The foulant using lime pretreated effluent was thought to be either a calcium sulphate or a calcium carbonate precipitates.

Flocculation with a sodium hydroxide/sodium carbonate mixture to circumvent high calcium values was attempted in order to prevent fouling of the reverse osmosis membrane. Organic removal by this pretreatment was low and the reverse osmosis tests showed rapid flux declines indicating that the organic components contributed to the fouling (Appendix A5.5) and that a calcium hydroxide precipitate was necessary to remove the organic foulants.

A further pretreatment step to remove the excess calcium from the effluent after lime flocculation and settling was investigated in a two stage process. Excess sodium carbonate was added in to the supernatant and the calcium was precipitated from solution as calcium carbonate. The calcium level after this second pretreatment stage was 5,8 mg/ℓ. Sodium concentrations were increased to 2 000 mg/ℓ from an initial value of 300 mg/ℓ. The precipitated solids in the two treatment stages were removed using a small bench scale cross-flow microfilter (CFMF) (Appendix A5.6). Table 2 shows the composition of the effluent before and after the two stage pretreatment. Hydrochloric acid was used to reduce the pH of the effluent to 7,5.

TABLE 2 PRETREATED FEED ANALYSIS (pH CORRECTED WITH HYDROCHLORIC ACID)			
Determinand	Feed as received	One stage pretreatment	Two stage pretreatment
pH	2,5	11,9	7,5
Conductivity	550	650	910
Total Solids	4 000	4 900	5 100
Total Organic Carbon	557	306	283
Sodium	629	604	2 148
Magnesium	141	0,5	0,6
Calcium	182	638	5,8
Chloride	1 369	1 364	2 582
All units mg/ℓ except pH and conductivity (mS/m)			

Further reverse osmosis trials with FilmTec and Du Pont elements using effluent pretreated in the two stage process showed little or no fouling. The specific flux data for the FilmTec membrane varied between 23 to 20 ℓ/m²h.MPa. A total of 1 000 litres of effluent was batch concentrated to 94 % water recovery during the course of the experimental run (Appendix A5.6).

The Du Pont element failed mechanically during the experimental run, probably owing to the high operating temperature (65 °C).

Figure 4 depicts the improvement in the operation characteristics of the membrane after each stage of pretreatment.

An investigation was made to determine whether the two stage separation pretreatment sequence using lime and soda ash could be adopted into a one stage separation process in which organic material and excess calcium could be removed simultaneously.

In the one stage separation the calcium organic complex formed upon lime addition, redissolved when sodium carbonate was added. The liberated calcium reacted with the carbonate to form calcium carbonate. Consequently the same level of organic removal was not achieved in the one stage process compared to the two stage process (Appendix A5.7).

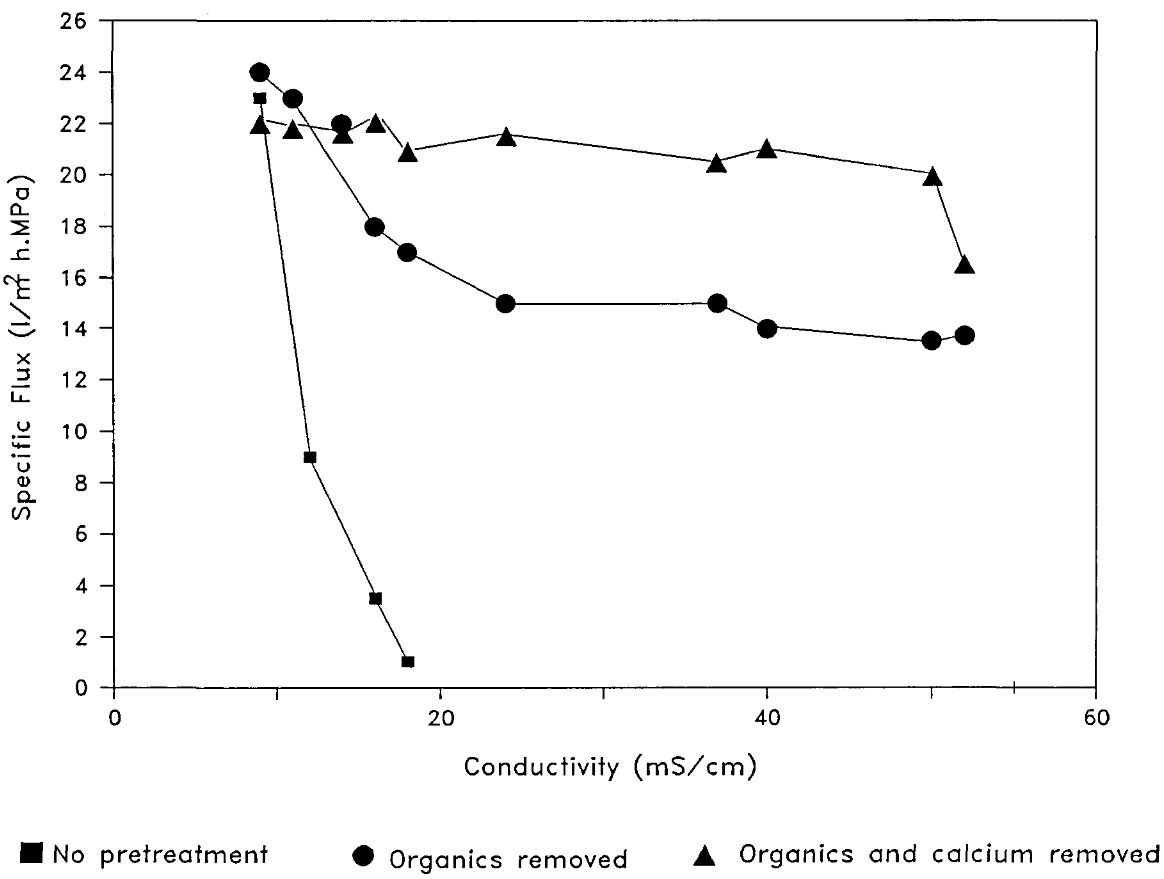

FIGURE 4
PLOT SHOWING THE SPECIFIC FLUX VS CONCENTRATION FOR UNTREATED AND PRETREATED BLEACH EFFLUENT

A two stage pretreatment process was required to remove organic carbon and calcium from the bleach effluent.

An analysis of the composite permeate and final concentrate of the FilmTec membrane at 93 % water recovery using a two stage pretreatment sequence is shown in Table 3.

An on-site pilot-plant study to confirm the bench scale results was considered necessary.

The FilmTec membrane was chosen for the on-site pilot-plant study at Enstra because of its superior rejection and flux characteristics.

The only major restriction on the use of this membrane was the possible presence of unreacted or dissolved chlorine which could have been carried over from the bleach plant. Chlorine degrades the membrane and a maximum exposure of 550 ppm hours of chlorine is allowed.

TABLE 3
BENCH SCALE RESULTS OF FILMTEC MEMBRANE AT 93 % WATER RECOVERY AFTER TWO STAGES PRETREATMENT AND pH CORRECTED WITH HYDROCHLORIC ACID

Determinand	Bleach	Pretreated RO feed	Brine	93 % point permeate	Composite permeate
pH	2,95	6,5	6,1	6,2	6,2
Conductivity	390	830	5 890	670	110
Total Solids	4 000	6 100	54 100	12 200	1 200
Total Carbon	570	252	2 177	115	34,3
Calcium	50	3	63	3,4	0,3
Magnesium	270	0,3	7,1	0,4	0,3
Sodium	340	2 143	18 600	4 275	489
Chloride	1 150	2 789	25 488	6 117	629

All units mg/ℓ except pH and conductivity (mS/m).

4 PILOT-PLANT DESIGN, COMMISSIONING AND OPERATION

4.1 Pilot-plant Design

A pilot-plant study was considered necessary to obtain the following information :-

(i) membrane flux versus water recovery,

(ii) permeate quality versus water recovery,

(iii) effect of feed velocity,

(iv) effect of feed temperature,

(v) effect of feed pressure,

(vi) control of fouling and chemical cleaning.

A tripartite agreement was entered into between the University of Natal (Pollution Research Group), the Water Research Commission and SAPPI to cover the hire costs of the RO rig from EPOC (Pty) Ltd. (Appendix A7.1). The hire period was from 1st January 1985 to 31st December 1985. This period was extended for a further 6 months because of commissioning problems (Appendix A7.2).

Various reverse osmosis pilot-plant design configurations were considered. A 2 : 1 module series taper configuration with 4 elements per module was the preferred configuration as it had the best production capacity (Appendix A8).

A pilot-plant comprising a prototype cross-flow microfilter single stage lime pretreatment unit (no calcium removal) followed by a series taper 2 : 1 reverse osmosis unit was constructed at the University of Natal to handle 4,2 m^3/h bleach effluent (Appendix A9).

SAPPI Research and Development Department was responsible for the following aspects.

(i) Site preparation, including services supply.

(ii) Provision of electricity, chemicals and effluent.

(iii) Provision of necessary storage tank, transfer pump and connecting pipe work between units.

(iv) Provision of plant operation and day-to-day supervision.

(v) Provision of minor maintenance.

(vi) Transport to and from site of the pilot-plant units.

The design options available for lime pretreatment of the effluent were :-

(i) simple batch flocculation,

(ii) continuous flocculation and settling followed by dual media filtration,

(iii) cross-flow microfiltration.

Options (i) and (ii) would require large volume tanks. Because of the expense involved in erecting tanks and the limited site area available, these options were not favoured. In addition, cross-flow microfiltration had been demonstrated as being capable of producing excellent quality filtrate with a relatively small filtration area. This method of pretreatment was considered the best option for the pilot-plant exercise.

The foulant encountered in the bench scale test work was thought to be either calcium sulphate or calcium carbonate. These precipitates could be controlled in a reverse osmosis environment by :

(i) Acid pH correction from pH 10,0 to pH 6,0 to prevent $CaCO_3$ precipitation. The recovered permeate was required to be at neutral pH and acid dosing after lime addition was necessary.

(ii) The addition of Calguard or similar crystal growth inhibitor to retard $CaSO_4$ precipitation.

The prototype cross-flow microfilter unit consisted of a 20 m long curtain of 20 tubes manifolded to form 5 parallel flow paths. The total length of each path was 80 m. The 20 individual tubes each had a diameter of 25 mm. The curtain was coiled in a spiral and hung from a frame which was suspended over the permeate collection tank. The permeate overflowed into the RO feed tank.

The cross-flow microfilter was over designed relative to the bench scale results to ensure a continuous feed to the reverse osmosis unit. No large buffer tank capacity between the units was incorporated into the initial design because of space limitations. No tube cleaning facilities were incorporated in the prototype CFMF unit. Both the CFMF and the RO pilot units were containerized for ease of transport and handling. The necessary electrical control systems were incorporated into the pilot-plant design (Appendix A9). The initial pilot-plant flowsheet is shown in Figure 5.

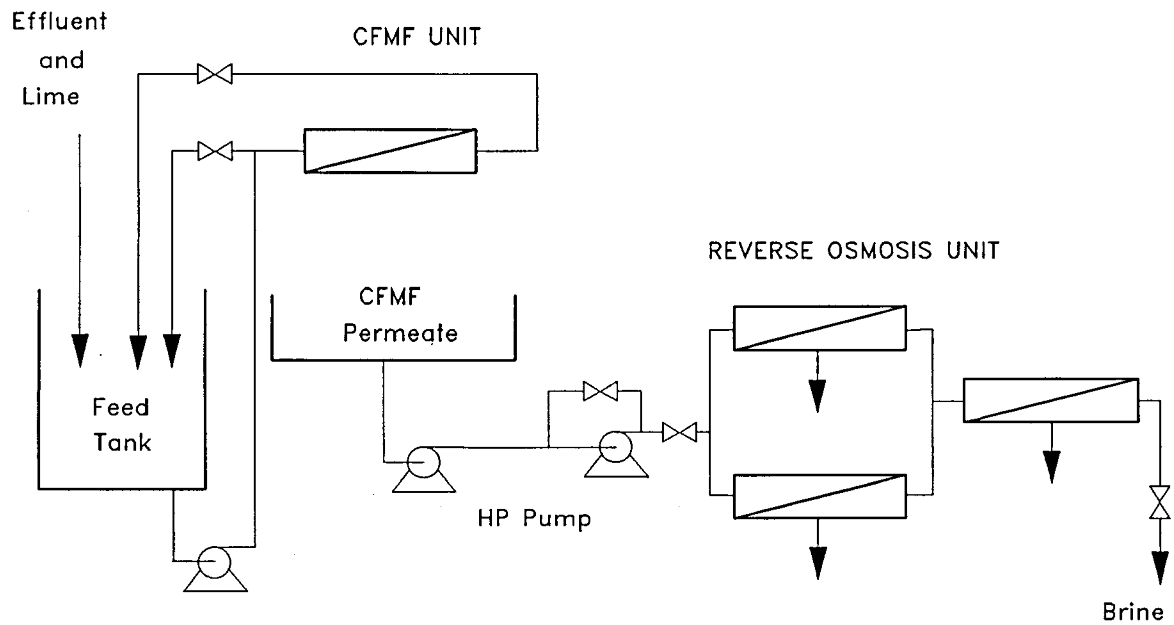

FIGURE 5
INITIAL PILOT-PLANT DESIGN

4.2 Pilot-plant Commissioning

Commissioning of the pilot-plant units at SAPPI Enstra started in November 1984.

A number of problems were encountered during the initial start-up phase (Appendix A10). Final commissioning was completed by the end of January 1985 and the day-to-day operation was handed over to SAPPI during February 1985.

4.3 Pilot-plant Operation

The reverse osmosis pilot-plant was designed to handle a continuous flow of 4,2 m^3/h of pretreated bleach effluent. The reverse osmosis and cross-flow microfiltration units were designed with a 15 minute buffering capacity between the units, consequently, in order to complete the RO test programme successfully the CFMF unit was required to produced 4,2 m^3/h or 135 ℓ/m^2h of treated bleach effluent.

Initial start-up of the CFMF unit showed marked flux declines which were not envisaged during the initial design. A decrease in flux from 350 to 25 ℓ/m^2h was monitored over 24 hours on start-up. The CFMF unit was unable to pretreat 4,2 m^3/h of bleach effluent for extended periods.

The philosophy followed was to try and improve the production of the CFMF unit by numerous system modifications (Appendix A10). Consequently the RO unit was not operated until a solution to the CFMF problem was found.

By October 1985, when no significant improvement in the CFMF operation had been made, a decision was taken to redesign the CFMF unit. Parallel work, on a separate Water Research Commission project at the University, had had success in maintaining a constant flux by installing a cleaning head. The SAPPI CFMF unit was redesigned as a linear system with a high pressure spray cleaning head. This was completed in January/ February 1986.

The installation of a cleaning head on the CFMF unit facilitated shut-down and start-up of the unit. Once the effectiveness of the cleaning head had been determined, the CFMF unit was run only for the purpose of producing feed for the RO unit. It was considered that the CFMF design data could be obtained at a later stage when the hire period of the RO unit had expired.

A problem that became significant once sufficient pretreated feed was available from the CFMF for reverse osmosis was the presence of free chlorine in the effluent.

The lengthy transport time between SAPPI Enstra and the University resulted in no free chlorine being present in the effluent during the initial bench scale test work. Laboratory tests at SAPPI showed a 2 to 3 day retention time was required to free the effluent of any residual chlorine.

The protection of the reverse osmosis membranes from chlorine degradation could have been achieved by the addition of a reducing agent (sodium bisulphite) to the effluent. However there were large fluctuations in the concentration of free chlorine in the effluent, making continuous dosing of reducing agent impossible without the installation of expensive process control equipment. In addition there was no control system on the bleach plant to regulate chlorine dioxide dosage.

It was decided that the safest way to operate the RO unit was on total recycle around a buffer tank. Fresh feed could only be transferred from the CFMF unit after it had been pH corrected and dosed to destroy free chlorine. The buffer tank would also alleviate the possibility of low production rates on the CFMF unit.

At water recoveries greater than 75 %, calcium sulphate fouling occurred if excessive sodium sulphite was used to destroy the free chlorine. Hence, if free chlorine in the bleach effluent was high, no transfer of effluent took place.

Running the RO unit on total recycle for extended periods did not achieve the purpose of the pilot-plant exercise, which was to expose the RO membranes to as much fresh effluent as possible. In addition, because of insufficient cooling capacity, it raised the temperature in the buffer tank above the recommended maximum operating temperature of the membranes so extended operation on total recycle was not possible.

The RO unit was run only under the supervision of an operator and only when the transfer of feed was possible.

Rapid fouling of the RO membranes occurred when exposed to the pretreated effluent. A flux decline from 60 ℓ/m^2h to 38 ℓ/m^2h over 10 hours was monitored on module 1 at 39 hours cumulative time (Figure 10) (Section 5.2). After 56 hours of operation, the specific flux of modules 1 and 2 was 11,8 $\ell/m^2h.MPa$ and 0,97 ℓ/m^2h for module 3.

An extensive organic and inorganic cleaning programme conducted over four days, restored the membrane fluxes to the original values. To limit further fouling of the membranes, the modules were flushed out with water at the end of each day (i.e. effluent was not allowed to stand in the module) and chemically cleaned after every 2 days of operation.

Laboratory tests at the University, using a simulated pilot-plant system, showed that the foulant (identified by X-Ray diffraction) was calcium oxalate and not calcium sulphate or calcium carbonate as originally assumed in the bench scale tests (Appendix A11.1).

Consequently it was decided to remove the excess calcium from the system prior to RO as in the bench scale test work (Appendix 11.2). A second CFMF unit was installed to remove calcium from the effluent using sodium carbonate. This was completed during April 1986.

The final pilot-plant design is shown in Figure 6.

A modified programme to utilize the remaining time on the pilot-plant as efficiently as possible was drawn up (Appendix A12).

Further RO test work, using effluent with a reduced calcium concentration, showed a substantial decrease in the rate of fouling. The membranes were allowed to stand in effluent overnight and chemical cleaning was practiced only after a total of five days of operation.

A guide to the day to day operation of the pilot unit is summarised in Table 4. The daily operation log for the pilot unit is presented in Appendix A13.

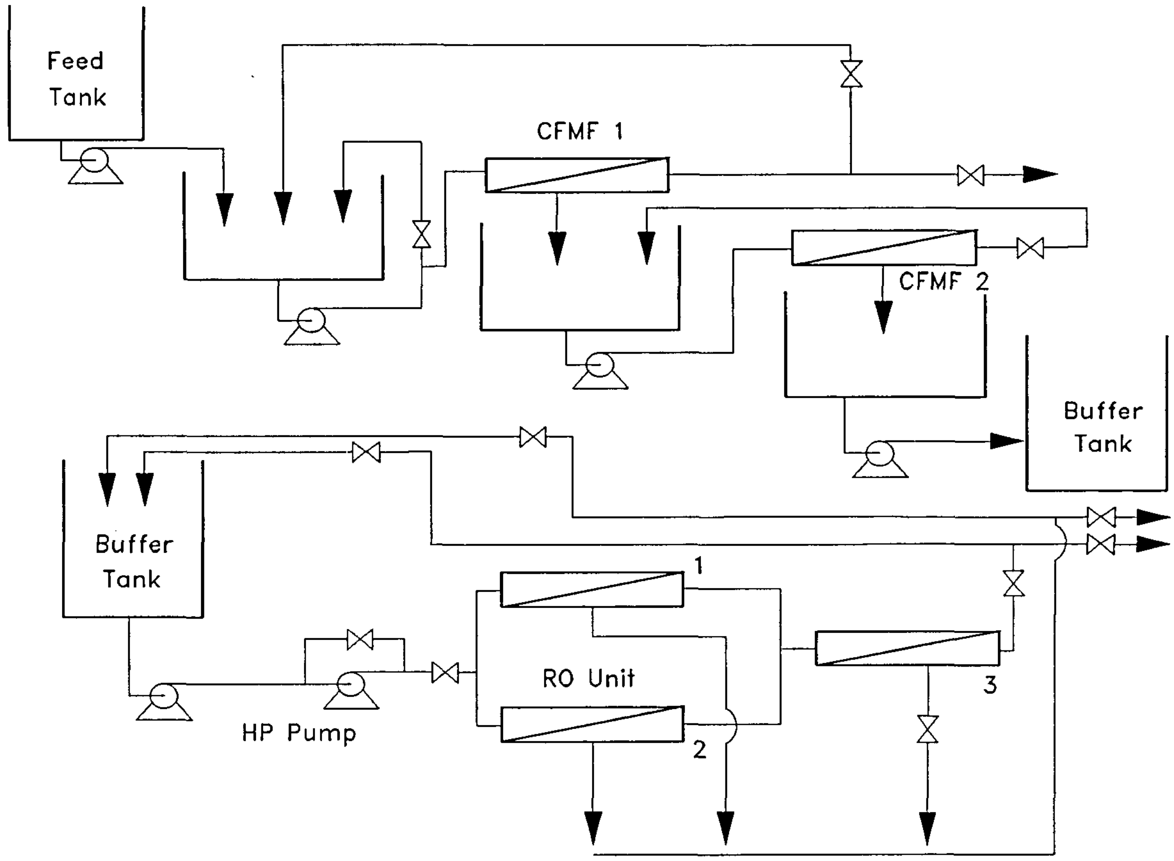

FIGURE 6
FINAL PILOT-PLANT DESIGN

TABLE 4
DAY TO DAY LOG OF PILOT PLANT OPERATION

	15-Oct	22-Oct	29-Oct	05-Nov	12-Nov	19-Nov	26-Nov	03-Dec	10-Dec	17-Dec	24-Dec	31-Dec	07-Jan	14-Jan	21-Jan	28-Jan	04-Feb	11-Feb
	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS
CFMF RUN									****	**				**** **	** **	**		******
R.O. RUN BLEACH																		*
FLUSH										**				*				* *
CLEAN																		*
SALT														*				*
CFMF DOWN						*****	*****	*****	*	* **	*****	*****	*****	*	* **	***	*****	*
R.O. DOWN						*****	*****	*****	*****	***	*****	*****	*****	****	*****	*****	*****	*
COMMISION					*******	*******	*******	*******										
CLOTH PLUGGED									. *	**						*		
CLOTH CLEANED										*			*****			**	****	
CLOTH REPLACED														*			*	
CLOTH REMANIFOLD																		*
BLEACH PLANT DOWN															* *			*
CHLORINE																		
CFMF PERM RATE LOW																		
MAINTENANCE-PUMPS						*****												*
-PIPING						*****	**						*	*				*
-ELECTRICS						*****												*
-CONTROLS							*****	*****					**	****		**		*
SYSTEM MODIFICATIONS	00000	00000	00000	00000													11111	

00000 PILOT PLANT MANUFACTURE COMPLETE 2/11/84

00000 PILOT PLANT TRANSPORT TO SAPPI 5/11/84

11111 INSTALL PREMIX TANK WITH ASSOCIATED PUMP AND PIPING

	18-Feb	25-Feb	04-Mar	11-Mar	18-Mar	25-Mar	01-Apr	08-Apr	15-Apr	22-Apr	29-Apr	06-May	13-May	20-May	27-May	03-Jun	10-Jun	17-Jun
	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS
CFMF RUN	****	*		*								**	******	*******	*******	****	****	*******
R.O. RUN BLEACH																		
FLUSH				*		*		*		*		*					*	
CLEAN			*															
SALT																		
CFMF DOWN	*	*****	*****	* ***	*****	*****	*****	*****	*****	*****	*****	** *	*			*	***	
R.O. DOWN	*****	*****	****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
COMMISION																		
CLOTH PLUGGED	*			*								*				*		
CLOTH CLEANED				*								*				*		
CLOTH REPLACED		**	*****							***	*****							
CLOTH REMANIFOLD		***		* *	*							** *	*			*	***	
BLEACH PLANT DOWN																		
CHLORINE												*		**	***	*		* *
CFMF PERM RATE LOW	****												****	*****	*****	****	*	*****
MAINTENANCE-PUMPS		*	***	*													***	
-PIPING			*	*									*				**	
-ELECTRICS		*																
-CONTROLS																		**
SYSTEM MODIFICATIONS					22222	22222	22222	22222	22222	22222	22222							

22222 INSTALL SCREENS FOR FIBRE REMOVAL,REMOVE CFMF PERMEATE TANK AND SUSPEND CLOTH FROM CONTAINER ROOF

22222 REMANIFOLD VALVE SYSTEM FOR MANUALLY OPERATED FLOW REVERSAL AND SPONGE BALL CLEANING

33333 MANUFACTURE AND INSTALL AIR OPERATED VALVE SYSTEM FOR AUTOMATED SPONGE BALL CLEANING

TABLE 4 (cont. i)

	24-Jun MTWTFSS	01-Jul MTWTFSS	08-Jul MTWTFSS	15-Jul MTWTFSS	22-Jul MTWTFSS	29-Jul MTWTFSS	05-Aug MTWTFSS	12-Aug MTWTFSS	19-Aug MTWTFSS	26-Aug MTWTFSS	02-Sep MTWTFSS	09-Sep MTWTFSS	16-Sep MTWTFSS	23-Sep MTWTFSS	30-Sep MTWTFSS	07-Oct MTWTFSS	14-Oct MTWTFSS	21-Oct MTWTFSS
CFMF RUN	***			* * ***	**** **		****				* * ***		* *	****	***			
R.O. RUN BLEACH					**		*											
FLUSH				*	*		*			*		*		*		*	*	*
CLEAN																		
SALT																		
CFMF DOWN	**	*****	*****	* *	*	*****	***	*****	*****	*****	* *	*****	** *	***	**	*****	*****	*****
R.O. DOWN	***	*****	*****	* ***	** *	*****	****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****
COMMISION																		
CLOTH PLUGGED	*							**			* *		*					
CLOTH CLEANED		****									* *		*					
CLOTH REPLACED						*		*										
CLOTH REMANIFOLD		*		* *	*		**	*										
BLEACH PLANT DOWN														*				
CHLORINE	**			*	**		* **				*		**		***			
CFMF PERM RATE LOW	***			* *	*									**	***			
MAINTENANCE-PUMPS						*****												
-PIPING				* *			*						* **					
-ELECTRICS												*****						
-CONTROLS				*														
SYSTEM MODIFICATIONS	33	33333	33333					44444	44444	44444						55555	55555	55555

44444 MANUFACTURE AND INSTALL COLUMN TO AIR STRIP FREE CHLORINE FROM BLEACH FEED

55555 DESIGN, MANUFACTURE AND INSTALL LINEAR CFMF UNIT

44444 REMOVE MONO-PUMP FROM CONTAINER AND REMANIFOLD

	28-Oct MTWTFSS	04-Nov MTWTFSS	11-Nov MTWTFSS	18-Nov MTWTFSS	25-Nov MTWTFSS	02-Dec MTWTFSS	09-Dec MTWTFSS	16-Dec MTWTFSS	23-Dec MTWTFSS	30-Dec MTWTFSS	06-Jan MTWTFSS	13-Jan MTWTFSS	20-Jan MTWTFSS	27-Jan MTWTFSS	03-Feb MTWTFSS	10-Feb MTWTFSS	17-Feb MTWTFSS	24-Feb MTWTFSS
CFMF RUN					***	****				*	***	***				*******	** ****	*******
R.O. RUN BLEACH					**											****	*	*****
FLUSH	*	*	*	*	*	*		*		*		*		*		* *	*	*
CLEAN																		
SALT																		
CFMF DOWN	*****	*****	*****	*****	**	*	*****	*****	*****	*** *	****	**	*****	*****	*****			
R.O. DOWN	*****	*****	*****	*****	***	*****	*****	*****	*****	*****	*****	*****	*****	*****	*****	* *	****	*
COMMISION																		
CLOTH PLUGGED					*	*				*		*						
CLOTH CLEANED					*	*				*	**	*	***					
CLOTH REPLACED																		
CLOTH REMANIFOLD											*							
BLEACH PLANT DOWN											*						*	
CHLORINE					*	**	*						* *		*		** *	
CFMF PERM RATE LOW						****					*	***						
MAINTENANCE-PUMPS																		
-PIPING																		
-ELECTRICS																		
-CONTROLS																		
SYSTEM MODIFICATIONS	55555	55555	55555	55555			66666	66666				77777	77777	77777	77777			

55555 INSTALL BUFFER TANK BETWEEN CFMF AND RO UNITS

66666 TEST VARIOUS CLEANING HEADS ON RIG AT UND

77777 MANUFACTURE AND INSTALL CLEANING HEAD

INSTALL HEAT EXCHANGER IN PERMEATE LINE FROM RO UNIT

TABLE 4 (cont. ii)

	03-Mar	10-Mar	17-Mar	24-Mar	31-Mar	07-Apr	14-Apr	21-Apr	28-Apr	05-May	12-May	19-May	26-May	02-Jun
	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS	MTWTFSS
CFMF RUN	*****	***		*****	****	*****				*****	*****	****	*****	*****
R.O. RUN BLEACH	* *	*		**	**	** *				***	** **	***	****	*
FLUSH	* *			**	**	**							*	
CLEAN		**	**	*	*	* *					*	*		*
SALT														*
CFMF DOWN		* *	*****		*		*****	*****	*****			*		
R.O. DOWN	***	** **	*****	** *	** *	* *	*****	*****	*****	**	*	**	*	* ***
COMMISION														
CLOTH PLUGGED														
CLOTH CLEANED														
CLOTH REPLACED														
CLOTH REMANIFOLD														
BLEACH PLANT DOWN		*	*				*		*					
CHLORINE	***		*		**					**		*		* ***
CFMF PERM RATE LOW														
MAINTENANCE-PUMPS														
-PIPING														
-ELECTRICS														
-CONTROLS			*											
SYSTEM MODIFICATIONS	88888	88888	88888				99999	99999	99999					

88888 RO FOULANT IDENTIFIED AS CALCIUM OXALATE

99999 MANUFACTURE AND INSTALL SECOND CFMF UNIT TO REMOVE EXCESS CALCIUM FROM THE EFFLUENT

5 PILOT-PLANT RESULTS

5.1 Cross-flow Microfiltration Unit

The unit arrived on site in October 1984 and was commissioned from October to December 1984. It was handed over to SAPPI in February 1985. Various system modifications were made to the CFMF unit between January 1985 and October 1985. The system modifications and experimental run numbers are tabulated below. The run dates shown are the dates of the test run following and preceding the system modifications.

(i)	Commissioning		-	13.1.85
(ii)	Run 1	14.1.85	-	30.1.85
(iii)	Install premix tank	30.1.85	-	12.2.85
(iv)	Run 2	12.2.85	-	17.2.85
(v)	Install screens for fibre removal + manual flow reversal + sponge ball cleaning	17.2.85	-	14.5.85
(vi)	Run 3	14.5.85	-	06.6.85
(vii)	Run 4	13.6.85	-	26.6.85
(viii)	Automated flow reversal + sponge ball cleaning	26.6.85	-	17.7.85
(ix)	Run 5	19.7.85	-	26.7.85
(x)	Linear CFMF + spray cleaning head	26.7.85	-	24.1.86
(xi)	Run 6	24.1.86	-	03.3.86

The CFMF results for the various runs are reported in Appendix A14.1 to A14.4 and are summarised in Figures 7, 8 and 9.

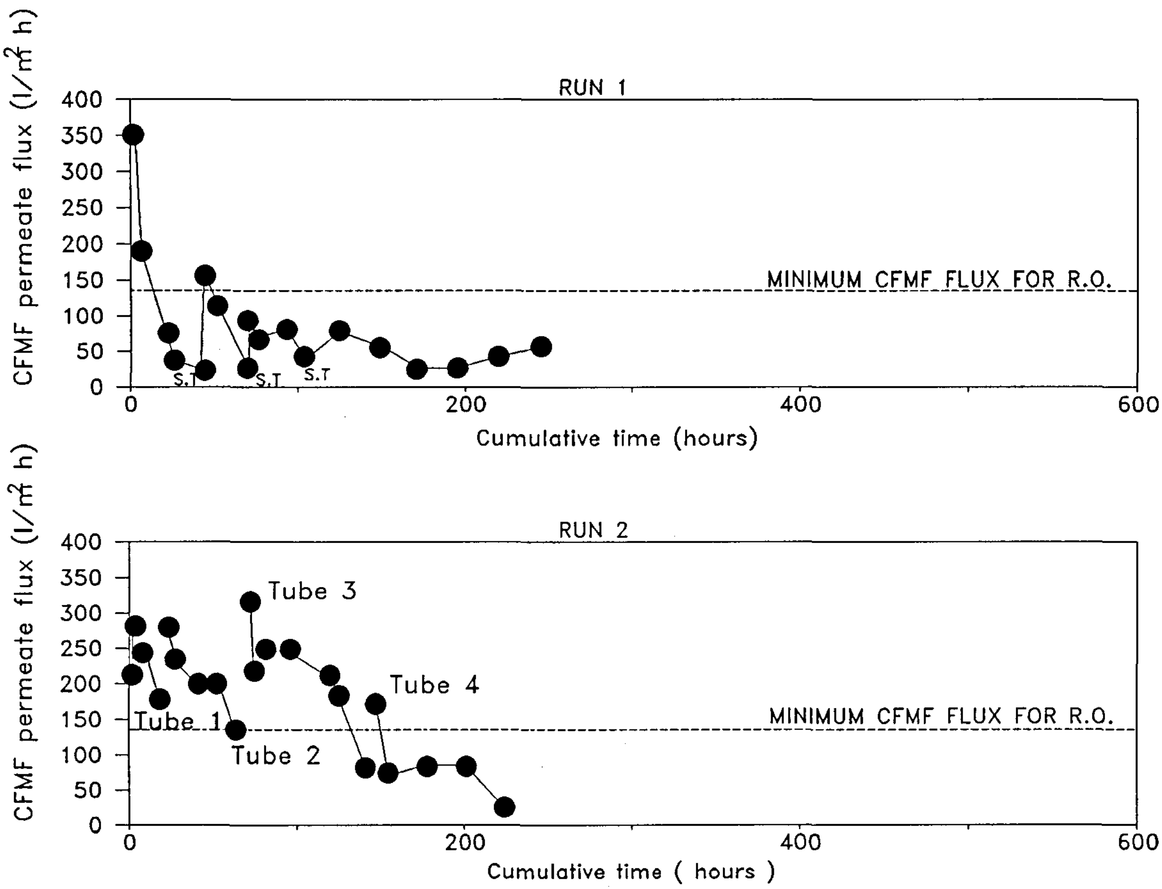

FIGURE 7
CROSS-FLOW MICROFILTER RESULTS (RUNS 1 AND 2)

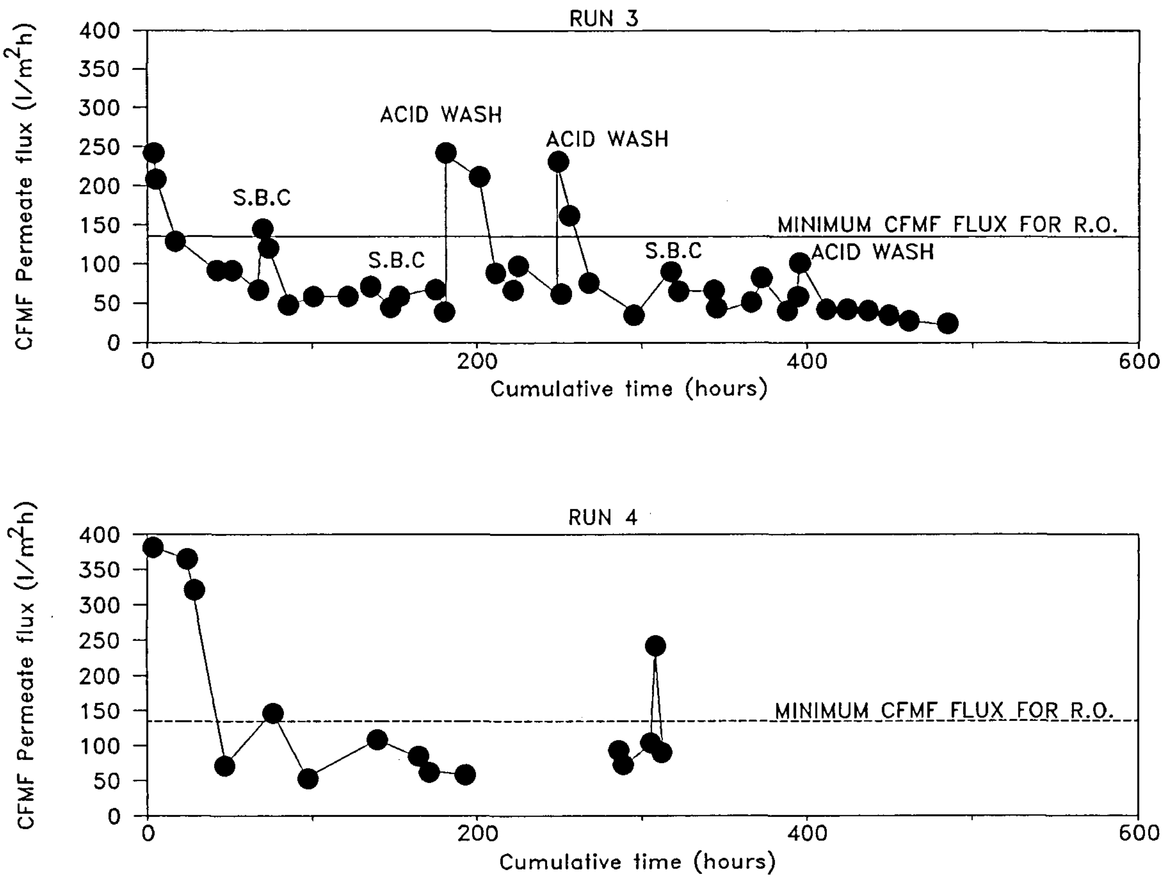

FIGURE 8
CROSS-FLOW MICROFILTER RESULTS (RUNS 3 AND 4)

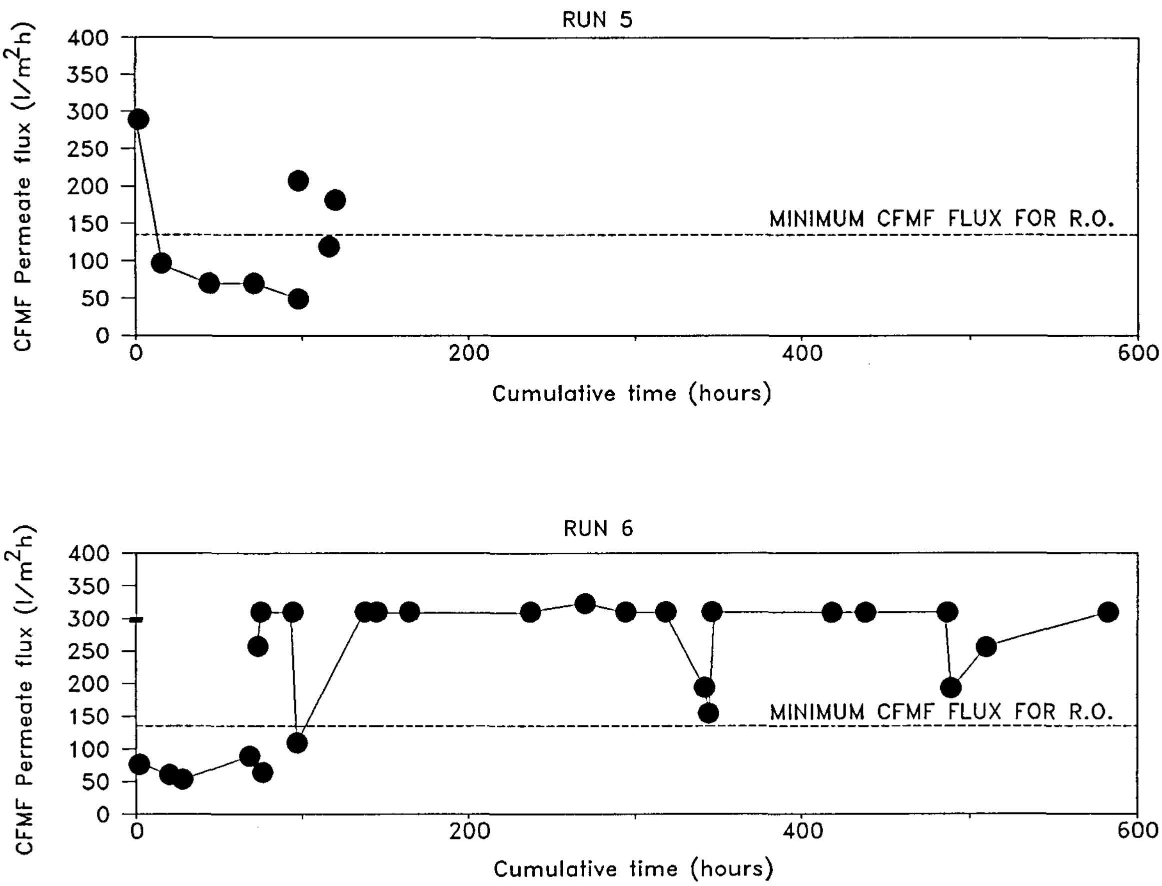

FIGURE 9
CROSS-FLOW MICROFILTER RESULTS (RUNS 5 AND 6)

With reference to Figures 7, 8 and 9 the following comments can be made :-

Run 1

The CFMF unit was started on the 1st bank of 5 parallel tubes. After the flux had declined from 350 ℓ/m^2h to 20 ℓ/m^2h the tube was shocked by switching the feed pump off and on. This dislodged some of the filter cake resulting in an increased filtration rate from 20 ℓ/m^2h to 135 ℓ/m^2h. When the flux had again dropped to 20 ℓ/m^2h the tube was shocked. From the plot it is clear that the effectiveness of shock treatment decreased with time.

Run 2

During this run successive filter tubes were brought on line as the flux decreased.

Run 3

Manual flow reversal with sponge ball cleaning (SBC) was attempted every hour to restore the rate of filtration. When SBC had no effect, the tubes were acid washed with a hydrochloric acid solution. This seemed to have a major effect but once on line, the flux dropped declined to previous values. The effect of acid washing decreased with each successive wash.

Run 4

Manual sponge ball cleaning and acid washing on a new CFMF cloth.

Run 5

An automated flow reversal system for continuous SBC was installed to stop the decrease in the rate of filtration which was suspected to occur overnight when no manual flow reversal was possible. A steady decrease in flux was still evident, SBC was not able to maintain high rates of filtration.

Run 6

A rapid flux decline is evident up to 73 hours after which the spray cleaning head was installed. Fluxes were maintained at 300 ℓ/m^2h with frequent cleaning. The low fluxes recorded are those before a wash cycle.

The rapid decrease in the rate of filtration of the CFMF unit in Runs 1 to 5 showed that plugging of the filtration pores of the filter cake by micro-particles and colloidal matter was occurring. Various attempts were made to improve the filtration rate. The installation of the spray cleaning head had a dramatic effect as seen in Run 6, where, with periodic cleaning of the cloth, it was possible to maintain the filtration rate.

An analysis of the CFMF permeate showed a TOC rejection of between 15 and 50 % based on bleach feed.

After the first liming stage for organic removal, calcium concentrations of over 1 000 mg/ℓ were recorded in the CFMF permeate. After the installation of the second CFMF unit, calcium concentrations of 37 mg/ℓ were achieved.

A typical analysis of the effluent before and after CFMF is shown in Table 5. Complete suspended solids removal was achieved.

The CFMF unit produced a permeate of excellent quality. The organic carbon and suspended solids removal was as expected from the laboratory and bench scale test work (Table 2).

The organic carbon removal varied according to the amount of calcium added to the bleach feed. A precipitate formed in the CFMF permeate on cooling.

TABLE 5 CROSS-FLOW MICROFILTER ANALYTICAL RESULTS 19th May 1986 (75 % Water Recovery)							
	pH	Cond mS/m	TS mg/ℓ	SS mg/ℓ	TC mg/ℓ	Mg mg/ℓ	Ca mg/ℓ
Bleach	3,0	434	3 664	24	603	124	130
CFMF Feed 1	9,5	414	4 938	428	545	113	316
CFMF Reject 1	9,8	424	5 502	1 056	524	138	334
CFMF Permeate 1	8,9	410	4 418	0	502	88	318
CFMF Feed 2	9,9	521	5 957	924	616	100	143
CFMF Reject 2	10,0	544	8 376	3 128	565	190	135
CFMF Permeate 2	9,7	521	4 996	40	539	104	37

5.2 Reverse Osmosis Unit

The actual run time of the RO unit on bleach effluent between February 1986 to June 1986 was 167 hours. The down time was accounted for by :-

(i) 16 days - excessive chlorine, no transfer of effluent possible,

(ii) 5 days - bleach plant down,

(iii) 11 days - cleaning RO membranes,

(iv) 15 days - system modifications,

(v) 15 days - laboratory investigation to determine the cause of fouling.

The RO results are tabulated in Appendix A15. A plot, showing the specific flux data against cumulative time is given in Figure 10 and indicates the state of the membrane during the test period.

Three distinct areas are defined :-

(i) calcium present, no cleaning,

(ii) calcium present, frequent cleaning,

(iii) calcium removed, periodic cleaning.

The flux decline shown during the first 10 hours of operation is a combined flux measurement. This did not give an indication of the state of the individual elements in each module. When individual module specific flux measurements were taken, fluxes of 5 $\ell/m^2h.MPa$ recorded on the last module showed that extensive fouling had taken place (Figure 10). Operation of the unit up to 60 hours showed the flux of the first two modules decreased during the day and returned to their original flux after standing overnight (possible osmotic cleaning effects occurring). The large flux decline of modules one and two between 40 and 60 hours indicated that precipitation of solids was occurring. This was aggravated by the high retention time of liquid in the buffer tank.

At 60 hours a major clean restored the fluxes to their original values. Thereafter the membranes were periodically flushed, and effluent not allowed to stand and cool in the modules. At 80 hours the second CFMF for calcium removal was installed.

The spot check analyses taken from the pilot-plant during the investigation indicated that the rejection performance of the plant was similar to that achieved on the bench scale tests.

When membrane fouling occurred only the permeate flux was affected, the membrane rejection remaining constant.

The pilot-plant unit (75 % WR) was capable of producing a permeate of suitable quality for recycle within the mill circuit.

The RO membrane gave excellent rejection performance on all species. Rejections between 96 to 98 % were recorded.

Spot samples of the feed and permeate streams were taken to ensure the membranes elements were performing according to their specifications.

Conductivity and flux measurements were taken periodically to ensure a specific flux calculation could be made to indicate the state of the membranes.

Table 6 shows a typical analysis of the feed, permeate and reject streams from the RO pilot unit. Other analysis are presented in Appendix A16.

Chemical cleaning of the reverse osmosis membranes using the manufacturer's prescribed cleaning solutions (Appendix A6.2) were effective in cleaning the fouled membranes and restoring fluxes. Sodium bisulphite solutions (500 mg/ℓ) were used to flush the membranes when they were not in use.

At the start of the pilot investigation, the permeate flux of a 5 g/ℓ NaCl solution was determined in order to provide baseline performance data. Appendix A17 describes the state of the membranes prior to and after the cleaning cycles. The 5 g/ℓ salt flux is also presented.

TABLE 6
REVERSE OSMOSIS RESULTS
19.5.86 (75 % Water Recovery)

	pH	Cond mS/m	TS mg/ℓ	SS mg/ℓ	TC mg/ℓ	TOC mg/ℓ	Na mg/ℓ	Mg mg/ℓ	Ca mg/ℓ	Cl mg/ℓ	SO_4 mg/ℓ
Bleach	3,0	434	3 664	24	603	596	530	124	130	1 390	112
RO Feed	5,3	598	5 486	20	331	286	2 864	20	118	2 116	327
RO Int	4,8	1 489	13 934	48	966	876	4 040	110	222	5 549	863
RO Reject	4,7	1 946	19 280	0	1 190	1 146	7 700	178	308	7 662	1 220
Perm 1	7,2	31*(95)	188 (96)	0	40 (88)	0 (100	120 (96)	2 (90)	8 (93)	56 (97)	0 (100)
Perm 2	7,0	25 (96)	168 (89)	56	36 (89)	26 (91)	80 (97)	1 (95)	3 (97)	52 (97)	0 (100)
Perm 3	6,3	52 (96)	362 (97)	0	39 (96)	28 (97)	180 (99)	1 (99)	4 (99)	-	0 (100)
Composite Perm	6,5	36	239	18	38	18	126	1	5	36	0
Target	-	42	355	2	58	51	51	12	12	134	-

*( ) % Point rejection.

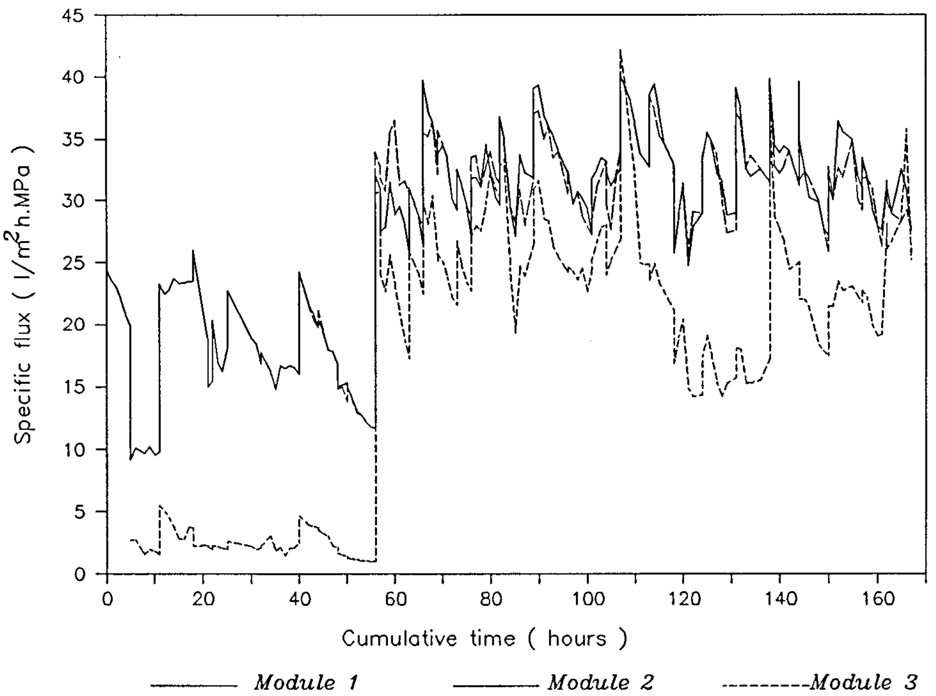

FIGURE 10
REVERSE OSMOSIS RESULTS
SPECIFIC FLUX VS CUMULATIVE TIME

6 PUBLICATIONS (APPENDIX A18)

A total of 10 publications and 12 conference papers have used information gathered during the course of this project.

6.1 Publications

1. GROVES, G.R., BUCKLEY, C.A., COX, J.M., KIRK, A., MACMILLIAN, C.D. and SIMPSON, M.P.J., 'Dynamic Membrane Ultrafiltration and Hyperfiltration for the Treatment of Industrial Effluents for Water Reuse', Desalination, **47**, pp. 305-312, 1983.

2. SIMPSON, M.P.J. and GROVES, G.R., 'Treatment of Pulp/Paper Bleach Effluents by Reverse Osmosis', Desalination, **47**, pp. 327-333, 1983.

3. GROVES, G.R. and BUCKLEY, C.A., 'Water Management and Effluent Treatment', Proceedings : Symposium on Forest Products Research International-Achievements and the Future, CSIR, Pretoria, South Africa, April 1985.

4. GROVES, G.R. and BINDOFF, A.L., 'Closed Loop Recycle and Treatment of Bleaching Effluents', Proceedings : Symposium on Forest Products Research International-Achievements and the Future, CSIR, Pretoria, South Africa, April 1985.

5. GROVES, G.R., BUCKLEY, C.A., SIMPSON, M.P.J., BINDOFF, A.L., TREFFRY-GOATLEY, K., ORBIN, A., NEYTZELL-DE WILDE, F.G. and DAVIES, C.J., 'Microfiltration Applications in the Treatment of Industrial Effluents', Proceedings : Symposium on Forest Products Research International-Achievements and the Future, CSIR, Pretoria, South Africa, April 1985.

6. BRABYN, N.R., SMITH, E.J., DAVIES, C.J., BINDOFF, A.L., GROVES, G.R. and OFFRINGA, G., 'Technical Performance Evaluation of Treatment Processes for the Recycling of Paper Machine Waste Water', Proceedings : Symposium on Forest Products Research International-Achievements and the Future, CSIR, Pretoria, South Africa, April 1985.

7. GROVES, G.R. and BINDOFF, A.L., 'Treatment of Pulp Mill Bleach Effluent for Water Reuse', IMIESA, pp. 33-40, August 1985.

8. BUCKLEY, C.A., BINDOFF, A.L., KERR, C.A., SIMPSON, A.E. and COHEN, D.W., 'The Use of Speciation and X-ray Techniques for Determining Pretreatment Steps for Desalination', Desalination, **66**, pp. 327-337, 1987.

9. BINDOFF, A.L., DAVIES, C.J., KERR, C.A. and BUCKLEY, C.A., 'The Nanofiltration and Reuse of Effluent from the Caustic Extraction Stage of Wood Pulping', Desalination, **67**, pp. 455-465, 1987.

10. SIMPSON, A.E., GROVES, G.R. and SIMPSON, M.P.J., 'Technical Note for the Examination of the Deposition of Dynamically Formed Hydrous Zirconium Membrane', Water SA, **15** (1), pp. 53-56, January 1989.

6.2 Conference Proceedings

1. SIMPSON, M.P.J. and GROVES, G.R., 'Treatment of Pulp/Paper Bleach Effluents by Reverse Osmosis', First World Congress on Desalination and Water Reuse, Florence, Italy, 23-27 May 1983.

2. GROVES, G.R., BUCKLEY, C.A., COX, KIRK, A. and SIMPSON, M.P.J., 'Pretreatment, Fouling and Cleaning in the Membrane Processing of Industrial Effluents', ACS-I&EC Symposium on Reverse Osmosis and Ultrafiltration, Philadelphia, USA, 26-31 August 1984.

3. GROVES, G.R., BUCKLEY, C.A., TREFFRY-GOATLEY, K., SIMPSON, M.P.J. and BINDOFF, A.L., 'Pretreatment, Fouling and Cleaning in the Membrane Processing of Industrial Effluents', ACS-I&EC Symposium on Reverse Osmosis and Ultrafiltration, Philadelphia, USA, 26-31 August 1984.

4. GROVES, G.R., TREFFRY-GOATLEY, K., SIMPSON, M.P.J., BINDOFF, A.L. and BUCKLEY, C.A., 'Pretreatment methods for Reverse Osmosis of Industrial Effluents', SA International Filtration Society, Johannesburg, South Africa, August 1984.

5. GROVES, G.R., TOWNSEND, R.B., SIMPSON, M.P.J., TREFFRY-GOATLEY, K. and BUCKLEY, C.A., 'Dynamic Membrane Treatment of Industrial Effluents', SA International Filtration Society Symposium, Johannesburg, South Africa, August 1984.

6. GROVES, G.R. and BUCKLEY, C.A., 'Water Management and Effluent Treatment', Symposium on Forest Products Research International-Achievements and the Future, CSIR, Pretoria, South Africa, April 1985.

7. GROVES, G.R. and BUCKLEY, C.A., 'Closed Loop Recycle and Treatment of Bleaching Effluents', Symposium on Forest Products Research International-Achievements and the Future, CSIR, Pretoria, South Africa, April 1985.

8. GROVES, G.R., BUCKLEY, C.A., SIMPSON, M.P.J., BINDOFF, A.L., TREFFRY-GOATLEY, K., ORBIN, A., NEYTZELL-DE WILDE, F.G. and DAVIES, C.J., 'Microfiltration Applications in the Treatment of Industrial Effluents', Symposium on Forest Products Research International-Achievements and the Future, CSIR, Pretoria, South Africa, April 1985.

9. GROVES, G.R. and BINDOFF, A.L., 'Practical Applications of Physico-Chemical Techniques to Industrial Effluent Treatment', Institute of Water Pollution Control, Biennial Conference, Durban, South Africa, 27-30 May 1985.

10. BUCKLEY, C.A., BINDOFF, A.L., DAVIES, C.J., JORY, N. and LYNN, D., 'The Treatment of Pulp Bleach Effluent Using Conventional Reverse Osmosis Membranes', Symposium on Effluent Treatment in the Chemical Industry (SA Chem. Inst.), Randburg, South Africa, 8 July 1986.

11. BUCKLEY, C.A., BINDOFF, A.L., KERR, C.A., KERR, A., SIMPSON, A.E. and COHEN, D.W., 'The Use of Speciation and X-ray Techniques for Determining Pretreatment Steps for Desalination', 3rd World Congress on Desalination and Water Reuse, Canada, France, 14-17 September 1987.

12. SIMPSON, A.E. and BUCKLEY, C.A., 'The Treatment of Industrial Effluents Containing Sodium Hydroxide to Enable the Reuse of Chemicals and Water', 3rd World Congress on Desalination and Water Reuse, Cannes, France, 14-17 September 1987.

7 ASSOCIATED PROJECTS AND CAPITAL INVESTMENT (Appendix 19 and 20)

During the course of this investigation there was input from concurrent Water Research Commission projects. These are listed in Appendix A19 together with the related fields of interest.

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Appendix A3.2	:	Hyperfiltration Studies X : Hyperfiltration with Dynamically-Formed Membranes. K.A. Kraus, A.J. Shor and J.S. Johnson, Jr. Desalination, **2**, pp. 243-266, 1967
Appendix A3.3	:	Filtration of Organic Solutes by Dynamically Formed Membranes. J.R. Kuppers, A.E. Marcinkowsky, K.A. Kraus and J.S. Johnson Separation Science, **2**(5), pp. 617-623, Nov. 1967
Appendix A3.4	:	Hyperfiltration XXI : Dynamically Formed Hydrous Zr(IV) Oxide-polyacrylate Membranes J.S. Johnson, R.E. Minturn, Jr. and P.H. Wadia Journal Electroanal. Chem. **37**, pp. 267-281, 1972
Appendix A3.5	:	Engineering Development of Hyperfiltration with Dynamic Membranes. Part 1 : Process and Module Development. D.G. Thomas and W.R. Mixon Desalination, **15**, pp. 287-306, 1974
Appendix A3.6	:	Engineering Development of Hyperfiltration with Dynamic Membranes. Part 2 : Brackish Water Pretreatment Pilot Plant. J.D. Sheppard and D.G. Thomas Desalination, **15**, pp. 307-323, 1974
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APPENDIX A18 : PAPERS AND PUBLICATIONS.

Appendix A18.1 : Treatment of Pulp/Paper Bleach Effluents by Reverse Osmosis.
M.P.J. Simpson and G.R. Groves
First World Congress on Desalination and Water Reuse, Florence, Italy, 23-27 May 1983

Appendix A18.2 : The Treatment of Industrial Effluents by Dynamic Membrane Technology.
G.R. Groves, C.A. Buckley, J.M. Cox, A. Kirk and M.P.J. Simpson
4th National Meeting of the South African Institution of Chemical Engineers, Potchefstroom University for CHE., Potchefstroom, 13-15 March 1984

Appendix A18.3 : Pretreatment, Fouling and Cleaning in the Membrane Processing of Industrial Effluents.
G.R. Groves, C.A. Buckley, K. Treffry-Goatley, M.P.J. Simpson and A.L. Bindoff
ACS-I&EC Symposium on Reverse Osmosis and Ultrafiltration, Philadelphia, USA, 26-31 August 1984

Appendix A18.4 : Pretreatment Methods for Reverse Osmosis of Industrial Effluents.
G.R. Groves, K. Treffry-Goatley, M.P.J. Simpson, A.L. Bindoff and C.A. Buckley
SA International Filtration Society, Johannesburg, South Africa, August 1984

Appendix A18.5 : Dynamic Membrane Treatment of Industrial Effluents.
G.R. Groves, R.B. Townsend, M.P.J. Simpson, K. Treffry-Goatley and C.A. Buckley
SA International Filtration Society, Johannesburg, South Africa, August 1984

Appendix A18.6 : Water Management and Effluent Treatment.
G.R. Groves and C.A. Buckley
Symposium on Forest Products Research International - Achievements and the Future, CSIR, Pretoria, South Africa, April 1985

Appendix A18.7 : Closed Loop Recycle and Treatment of Bleaching Effluents.
G.R. Groves and C.A. Buckley
Symposium on Forest Products Research International - Achievements and the Future, CSIR, Pretoria, South Africa, April 1985

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Symposium on Forest Products Research International - Achievements and the Future, CSIR, Pretoria, South Africa, April 1985.

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G.R. Groves and A.L. Bindoff
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Appendix A18.10 : The Treatment of Pulp Bleach Effluent Using Conventional Reverse Osmosis Membranes.
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Appendix A18.12 : The Treatment of Industrial Effluents Containing Sodium Hydroxide to Enable the Reuse of Chemicals and Water.
A.E. Simpson and C.A. Buckley
3rd World Congress on Desalination and Water Reuse, Cannes, France, 14-17 September 1987.

Appendix A18.13 : Dynamic Membrane Ultrafiltration and Hyperfiltration for the Treatment of Industrial Effluents for Water Reuse.
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Desalination, 47, pp. 305-312, 1983.

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Appendix A18.15 : Water Management and Effluent Treatment.
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Appendix A18.17 : Microfiltration Applications in the Treatment of Industrial Effluents.
G.R. Groves, C.A. Buckley, M.P.J. Simpson, A.L Bindoff, K. Treffry-Goatley, A. Orbin, F.G.N.-de Wilde and C.J. Davies
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Appendix A18.18	:	Technical Performance Evaluation of Treatment Processes for the Recycling of Paper Machine Waste Water. N.R. Brabyn, E.J. Smith, C.J. Davies, A.L. Bindoff, G.R. Groves and G. Offringa Proc. Symposium on Forest Products Research International - Achievements and the Future, CSIR, Pretoria, South Africa, April 1985.
Appendix A18.19	:	Treatment of Pump Mill Bleach Effluent for Water Reuse. G.R. Groves and A.L. Bindoff IMIESA, pp. 33-40, August 1985.
Appendix A18.20	:	The Use of Speciation and X-ray Techniques for Determining Pretreatment Steps for Desalination. C.A. Buckley, A.L. Bindoff, C.A. Kerr, A. Kerr, A.E. Simpson and D.W. Cohen Desalination, **66**, pp. 327-337, 1987.
Appendix A18.21	:	The Nanofiltration and Reuse of Effluent from the Caustic Extraction Stage of Wood Pulping. A.L. Bindoff, C.J. Davies, C.A. Kerr and C.A. Buckley Desalination, **67**, pp. 455-465, 1987.
Appendix A18.22	:	Technical Note for the Examination of the Deposition of Dynamically Formed Hydrous Zirconium Membrane. A.E. Simpson, G.R. Groves and M.P.J. Simpson WaterSA, **15**(1), pp. 53-56, January 1989.
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