EXECUTIVE SUMMARY

1.1 INTRODUCTION

The development of inert durable membranes over the past three decades saw pressure-driven processes, like microfiltration, ultrafiltration and reverse osmosis, develop into viable options for the treatment of large volumes of industrial effluents from various origin. The chemical stability and physical properties of membrane polymers, such as poly(ethersulphone) (PES), made the design and manufacture of membrane plants, capable of clarifying extremely reactive and "hostile" effluents, possible. The most challenging obstacle in the way of full implementation of modern pressure-driven filtration processes, however, is the fouling phenomenon, an inherent consequence of any membrane filtration process used for the clarification of industrial effluent or polluted water.

The diversity of the effluents and water being treated by pressure-driven filtration processes rules out any single method as a total solution to membrane fouling. This problem is usually addressed by a combination of effluent pre-treatment and differential flow techniques in conjunction with chemical and physical cleaning of the fouled membranes. For the development of the most effective physical and chemical membrane cleaning methods, information on the physical and chemical properties of membrane foulants is important. During the past decade the membrane research group at the University of Stellenbosch, comprising the Institute for Polymer Science and the Department of Biochemistry, focussed on foulant characterisation and foulant removal from UF membranes used in industrial effluent treatment.

1.2 OBJECTIVES

In a previous WRC project (WRC no. 660) methods for effluent and foulant characterisation, membrane cleaning and membrane pre-treatment techniques were developed and successfully applied to membranes fouled by pulp and paper effluent under laboratory-scale conditions. This effluent came from cascading dams at the Mondi Kraft paper mill at Piet Retief, which were part of the effluent pre-treatment process prior to ultrafiltration. The reason for the investigation into this specific effluent was the deterioration in the performance of the membrane plant due to extensive fouling. During these studies spectrophotometric analyses showed that pulp and paper effluent, from the Mondi Kraft mill, contained unsaturated aromatic compounds and that ultraviolet-visible spectroscopy (UV-Vis spectroscopy) could be used to estimate the concentration of these potential foulants in the effluent. Combining pure-water flux (PWF) measurements and phenolic staining techniques with UV-Vis analyses, foulant adsorption onto PES ultrafiltration membranes was studied and partial identification of foulants was possible. Pre-coating of the membranes with Pluronic® F108 resulted in a significant reduction in foulant adsorption over a 90 h filtration period under cross-flow conditions, and the flux through fouled membranes was successfully restored by cleaning with the non-ionic detergent Triton X100® and sponge balls. To build on and extend the previous work, the initial aims of this project were the following:

1. Development of a pilot scale filtration unit at Weir Envig (Pty) Ltd. (Paarl).
2. Characterisation of dam effluent to confirm previous results.
3. Implement membrane cleaning techniques developed under laboratory conditions at the pilot plant.
4. Evaluate cleaning techniques in terms of cleaning efficiency and cost effectiveness.
5. Implement non-covalent membrane pre-treatment techniques on a pilot scale.
6. Evaluate the feasibility of membrane pre-treatment techniques on the basis of cleaning frequency and cost effectivity.
7. Transfer technology to the industry for large-scale implementation.

As mentioned earlier, the performance of the membrane plant at Piet Retief deteriorated after an initial period of normal operation. This deterioration was subsequently ascribed to the presence of reduced sulphur compounds in the dam effluent. It was concluded that sulphur reducing bacteria in the dams were responsible for sulphur production. The "*sulphur problem*" prompted by-passing of the dams and feeding of paper machine effluent directly from the pulp and paper factory to the ultrafiltration plant. This change in feed composition resulted in a rapid and total blockage of the membranes due to the presence of fibres in the effluent. To overcome this problem the installation of a dissolved air flotation (DAF) clarifier was commissioned. Lower operating fluxes were, however, attained with the clarified paper machine effluent (DAF product) than with the dam effluent. This prompted an investigation into a decrease in the operating fluxes.

In addition to the installation of the DAF clarifier, changes in the paper production process, the mill, and the pre-treatment regimes implemented before flotation, also altered the composition of the UF-feed. These changes to the UF-feed necessitated a shift in emphasis from the goals originally set for the current project. It was decided by the Steering Committee that the group at Stellenbosch would take a more fundamental approach to solving the fouling problem, while the work at the mill would take a incremental improvement approach and that progress in each approach could complement the other in search of an effective solution to the fouling problem. The altered aims for the Stellenbosch group were:

1. Characterisation of the DAF effluent and foulants on PES membranes using UV-Vis spectroscopy, gel permeation chromatography (GPC), inductively coupled plasma (ICP), atomic force microscopy (AFM) and scanning electron microscopy (SEM).
2. Static fouling of PES membranes with flocculants and coagulants used in the pre-treatment of paper machine effluent prior to DAF-clarification, to determine their respective roles in fouling.
3. Characterisation of membrane foulants on membranes from a flat-sheet test rig that was used to test different approaches to fouling reduction at the mill.

1.3 DISCUSSION

The laboratory analyses, carried out at the University of Stellenbosch, were designed to answer the following questions:

1. What are the fouling characteristics of the DAF effluent?
2. What is the influence of flocculants and coagulants, added to the effluent to enhance the DAF process, on membrane performance?
3. What are the most obvious fouling characteristics of the effluent prior to UF, and do the DAF clarifier and microstrainer add to the fouling potential of the effluent?
4. How is the character of the membrane surface influenced by foulant deposition?

These studies, and the results obtained, are given in **Chapters 2** to **5** of this report. The conclusions drawn from these results can be summarised as follows:

Unused membranes statically fouled with DAF effluent showed a reduction in PWF. The reduction in PWF was attributed to the adsorption of the organic compounds present in the effluent to the surface of the hydrophobic PES membranes. Pluronic® F108 coated membranes fouled with DAF product yielded a slightly higher PWF compared to that obtained for unused Pluronic® F108 coated membranes. Coating membranes with Pluronic® F108, however, had no apparent advantage for fouling prevention and productivity enhancement.

Static fouling experiments carried out on the flocculants and coagulants used during the papermaking process in the Kraft mill showed that none of the agents adsorb irreversibly onto the membranes. The results also showed that none of the flocculants and coagulants used in the DAF clarifier fouled the UF membranes.

Effluent analyses showed that all effluents analysed contained aromatic compounds and unsaturated polymers which could act as potential foulants. The same type of compounds were indicated in all the samples (liquid and membrane) analysed and lignosulphonate appeared to be the main constituent. The pH of the solution had a marked effect on the UV-Vis characteristics of the compounds in the effluent with a shift to higher absorbance maxima being induced at elevated pH. These changes can be ascribed to de-ionisation of functional groups (carboxylic and phenolic) on the foulants present in the effluent. Precipitation was observed in effluent samples with an elevated pH when left undisturbed for 2 h. This increase in turbidity could be attributed to complex-formation between negatively charged foulants and cations present in the effluent. ICP analyses confirmed the presence of high levels of calcium in the effluent. Complex formation, and a subsequent increase in turbidity, could be enhanced by the addition of calcium and reversed by the addition of EDTA, a the chelating agent. These results supported the idea that polymeric substances in the effluent complexed metal ions at elevated pH. Further GPC analyses of the effluent at different pH and calcium concentrations confirmed conclusions drawn from the UV-Vis data and indicated the formation of high molecular mass complexes at pH 13. From these studies it is apparent that any future cleaning regimes or fouling prevention measures will be more successful if these properties of the effluent are considered.

AFM analyses of unfouled and fouled membranes, showed a distinct difference in the surface roughness of the two samples. Significant deposits of foulants could be observed on membranes, received from the mill at Piet Retief. These results were confirmed by SEM analyses which showed fibres as prominent components of the fouling layer. Indicating that a more efficient microstrainer should be used after the DAF clarifier.

A large number of experiments were carried out at the Piet Retief mill. These experiments and the results obtained are given in **Chapter 6** and conclusions to this part of the study may be summarised as follows:

- The DAF product had the same fouling tendency regardless of the pre-treatment program being used to promote flocculation and scavenging of suspended solids in the effluent. The 30 μm microstrainer, installed to remove residual fibres, had limited success as it did not change the fouling tendency of the DAF product. These results are supported by the laboratory experiments carried out in Stellenbosch.

- The UV-Vis-analyses of the effluent showed pH-associated changes in character due to ionisation. Increasing the pH of the effluent feed to the test rig from 4.5 to 10 reduced the rate of membrane fouling.

- Membranes used for the filtration of effluent, with added black liquor, showed a significant flux recovery after cleaning in place (CIP). Unfortunately, the operating fluxes decreased considerably when filtration was resumed. Sodium lignosulphonate, a component of black liquor, was thought to be responsible for the lower fluxes. Comparative UV-Vis analyses confirmed the presence of lignosulphonate in the effluent.

- Attempts to remove foulants from the effluent stream by means of activated carbon, ion exchange resin or PS beads were unsuccessful.

- The use of Triton X-100®, a non-ionic surfactant, as a CIP reagent in some instances increased the operating flux after CIP to values higher than that of the original membrane.

- Negatively charged polysulphone membranes, obtained from Osmonics, were less susceptible to fouling. The 5 kDa molecular mass cut-off (MMCO) Osmonics membrane was operated successfully for several days without a significant loss in flux, indicating that hydrophilic or negatively charged membranes withstood membrane fouling more effectively than hydrophobic PES membranes, under the same operating conditions.

- Mechanical cleaning of the PES membrane surface with spongeballs proved to be one of the most effective and successful methods to prevent flux loss caused by fouling.
- Pre-treatment of the PES membranes with Pluronic® F108, a non-ionic surfactant, only marginally reduced membrane fouling. The pattern of the operating flux loss with time, however, remained unchanged.
- High operating fluxes were obtained with the dam effluent. This could be attributed to the very long retention time and favourable anaerobic conditions that allowed for the partial biodegradation of the organic material and complete clarification of the dam effluent to very low levels of suspended solids. The flux loss experienced with dam effluent after several CIP sessions was, however, the highest for all the experiments. It was found that the dam effluent contained reduced sulphur compounds that could not easily be removed from the membranes.
- UV-Vis analysis provided limited information on the chemical composition of the foulants present in the effluent. The majority of the samples analysed showed absorbance in the UV region, indicating that the presence of aromatic compounds in the effluent. Lignosulphonate was found to be a major constituent in the various effluent samples. It is, however, interesting to note that the UV-Vis spectra of most of the membrane extracts did not show the absorbance maxima below 210 nm that was seen for the paper machine effluent, DAF and microstrainer products as well as the lignosulphonate. This observation indicates that the compounds absorbing at the lower wavelengths (unconjugated olefinic compounds) did not foul the membranes to the same extent as the aromatic substances with absorbance maxima between 230 and 400 nm. To prove this hypothesis conclusively, however, further extensive experimentation is needed.

1.4 RECOMMENDATIONS

From the results obtained in laboratory studies as well as work done on the test rig at the Piet Retief mill the following recommendations for future research can be put forward:

As elevation of the pH of the effluent feed to the UF plant reduced the rate and degree of membrane fouling considerably. Future operations should be at pH 10. Precipitation at elevated pH values greater than 10 resulted in the clarification of the effluent and consideration could be given to the inclusion of an alkaline pH period before UF. Chelating agents can be added to the DAF clarifier to remove any divalent metal ions, e.g. Ca^{2+}, which promote membrane fouling.

- The use of an anionic surfactant as a membrane pre-coat or hydrophilic membranes should be investigated.
- The use of a microstrainer with smaller apertures to remove any residual fibres from the DAF product, should be considered.

1.5 CONCLUSION

Large-scale effluent treatment, as described in the previous sections, requires the successful and sustainable application of sophisticated technology, like membrane UF. To meet this challenge, highly trained and skilled personnel are needed to ensure optimal operation and maximum output. Circumstances and operating conditions can, however, change and compromise the output of the plant as was the case with the fouling problem experienced at the UF plant in Piet Retief. The solution to the problem required skilled personnel and specialised research facilities which the plant did not have. Under these circumstances the involvement of universities in collaboration with the industry allowed for the continuous operation of the mill, while the problem was being addressed. This collaboration allowed for the exchange of experience and information obtained during laboratory studies and the actual operation of the plant under production conditions. The success of this project can largely be attributed to the co-operation of Mondi Kraft, specifically the personnel at the mill, who collaborated and exchanged ideas with the research groups at the Universities of Natal and Stellenbosch. In addition to the fostering of excellent cooperation betweeen industry and academic institutions, this project also allowed for the training and development of three historically disadvantaged individuals. Mr Victor Sibiya, working at the mill in Piet Retief as part of the Mondi team, gained invaluable experience in membrane technology and trouble shooting. In Stellenbosch ms Ayesha Hansa, formerly from the ML Sultan Technikon, was involved in membrane and effleuent characterisation while mr Garth Domingo was involved as one of the pricipal investigators of the project. Mr Domingo, who was part of the research team from the start of the project, will also be submitting his masters thesis in December 2001.