RESEARCH INTO THE TREATMENT OF WOOL SCOURING EFFLUENTS

Report to the
WATER RESEARCH COMMISSION
by
GUBB & INGGS LTD
and
POLLUTION RESEARCH GROUP
DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF NATAL

WRC Report No 161/1/94

FINAL REPORT

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WOOL SCOURING EFFLUENTS

by

Gubb & Inggs Limited
Hendrik van Eck Drive
Uitenhage
6230

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Department of Chemical Engineering
University of Natal
Durban, 4001, South Africa

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Gubb & Inggs Project & Development Manager	:	Dr DWF Turpie
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EXECUTIVE SUMMARY

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EXECUTIVE SUMMARY

1.1 BACKGROUND AND MOTIVATION FOR THE PROJECT

Even though the contaminants of the wool fleece are of no great concern to anyone while they are being carried about by the sheep itself, the liquid wastes emanating from the commercial scouring of such wool have long been regarded as highly polluting and difficult to treat. The components themselves are highly variable by virtue of their origins, and an effluent is thus produced having different ratios of its constituents from hour to hour.

While almost all conceivable methods of treating waste waters have been applied to scouring wastes at one time or another, with varying degrees of success, most are highly capital intensive, or are associated with high running costs, or are not feasible in certain locations or countries for one reason or another. Research into the treatment of such effluents is, therefore, on-going in various parts of the world.

The relatively new approach, pioneered by the University of Natal, and involving the application of dynamic ultrafiltration, appeared to hold promise as a new alternative technology for the treatment of wool scouring effluent which could be of value to the local industry, and even have application in a wider field. It was necessary, however, to evaluate this technology in an industrial environment. In this context the firm of Gubb & Inggs Limited was ideally placed. Not only did it have one of the largest mills for the processing of raw fibre in the Southern Hemisphere, and an involvement in scouring a very wide selection of fibres, but it was prepared to cooperate and collaborate with the University of Natal in trying out this new technology. Furthermore, the Water Research Commission was prepared to sponsor the project financially. Accordingly, a Contract was entered into in 1985 involving the Water Research Commission, the University of Natal (Pollution Research Group), Binnie & Partners (Consultants) (later Steffen Robertson & Kirsten) and Gubb & Inggs to pursue this new approach.

1.2 OBJECTIVES

The detailed objectives of the project were as follows:

(i) to determine the technical feasibility of dynamic ultrafiltration in the treatment of scouring effluent for water re-use at high water recoveries.

(ii) to evaluate the reuse of the reclaimed water in the production environment.

(iii) to evaluate the processing performance and the cost effectiveness of the system.

(iv) to evaluate the mechanical performance of the system.

(v) to develop estimates of the nett savings in water recycle, energy conservation, waste treatment and possible chemical recovery.

(vi) to develop a detailed design for the full-scale treatment of wool scouring effluents.

(vii) to progressively review the achievements of these objectives, and to ensure their successful completion.

1.3 SUBSEQUENT CHANGE IN DIRECTION

While much useful data emerged during the first few years of the project, the system was not considered viable when conducted on scouring effluent. In 1990 it was agreed by all parties to suspend research in this direction, and to change over to the treatment of dirty rinse water from the rinse bowls. At the same time it was agreed to integrate the firm's biological degradation ponds into the water and effluent loop.

1.4 SUMMARY OF MAJOR RESULTS AND CONCLUSIONS REACHED

1.4.1 Laboratory & Pilot-plant Trials

These indicated that dynamic membranes of the hydrous zirconium (iv) oxide type could be used successfully to treat scour effluent. Rejections of 100%, over 92% and over 85% could be obtained for grease, total organic carbon and total solids, respectively. Furthermore, 85% of the original feed could be recovered for potential re-cycle.

1.4.2 Trials Involving Modular Demonstration Plant on SCOUR EFFLUENT

These trials illustrated the need for membrane re-formation as the modules became progressively fouled. Initially, re-membraning was carried out at the University of Natal on a 2-monthly cycle, but fouling was still a problem. Subsequently re-membraning was carried out on site and the problem was reduced. While fluxes could be maintained in the short term while plant operation was continuous, unscheduled stoppages had a marked effect on performance. It was concluded that cooling of the liquor in the modules resulted in module fouling. Failure of one of the two high-pressure feed pumps, which were connected in parallel, also resulted in serious fouling due to the halving of the cross-flow velocity from 2 to 1 m/s. In this case a subsequent return to high velocity did not restore the flux within a reasonable time span.

Removal of the foulants and stripping of the dynamic membrane was accomplished by circulating one-molar solutions of sodium hydroxide, sodium hydroxide/hydrogen peroxide mixture, and nitric acid, in turn, through the module at 80 °C. Because the foulant was embedded or chemically bonded in the matrix of the membrane/substratum significant flux restoration was not possible without stripping followed by membrane re-formation.

Unfortunately the quality of the permeate was at all times too poor to be acceptable by management for re-use in the rinsing of the scoured wool product, and consideration of a tertiary treatment plant was ruled out on economic grounds.

1.4.3 Trials Involving Modular Demonstration Plant on RINSE EFFLUENT

In the treatment mode which involved treatment of the dirty rinse effluent as opposed to the effluent produced from the earlier, highly contaminated, scouring bowls not only was the treatment itself successfully accomplished from a technical point of view, but re-use of the processed water enabled the factory to reduce its normal water use by half and the quality of the wool product passed all the firms requirements.

Individual flux rates for the membranes varied widely and were shown to decline rapidly with time. The effects of suppression of bacterial growth on flux rates were inconclusive, and flux decline was still marked. Membranes needed to be stripped around once every 10 days to maintain fluxes at a reasonable figure. This required frequent utilisation of skilled personnel in the factory who, in a production environment, were not always available. As a consequence it was decided to design and build an automatic membrane formation plant.

With the automated membrane formation plant in operation several studies were carried out.

It was found that there was a relatively high between-module flux variability. Furthermore some modules required cleaning more frequently than others. Inherent variations in pore size and available pore area may have been contributory factors, but it was suspected that some of the foulant remained as an integral part of the substrate.

In contrast to observations on the scour effluent, no deterioration in flux could be observed during a specific concentration cycle, in spite of a four-fold increase in the levels of grease and suint and a seven-fold increase in dirt.

Treatment of the modules by total immersion in concentrated sulphuric acid for up to three hours resulted in a dramatic improvement in flux, and such treatment was thereafter implemented on a regular basis.

The membranes rejected all the dirt, and about two thirds of the grease and suint. Conductivity was reduced by 44%, turbidity by 99%, COD by 89% and absorbance from 92% to 96% at wavelengths of 350nm to 700nm. The high colour rejection was considered of special importance in the context of wool washing.

Consumption of Town's Water was monitored on the specific washline on which the project was carried out for some 50 operational days. The results showed that, as a result of the recycling of permeate to the rinse bowls, in the context of the integration of water from the firm's biological ponds into the scouring loop, Town's water use was reduced by approximately 50%. (The high residual detergency and alkalinity of the water from the biological ponds has found excellent use both in the firm's scouring and carbonising operations while at the same time reducing the firms total use of soda ash by approximately 40%).

Membrane fouling again become serious during 1991/2, and although relatively high fluxes could be obtained by pre-treatment with sulphuric acid, they plunged to low levels in a short period. The reason for this can be traced to the firm's increased use of water from the biodegradation ponds during the height of the drought in the Eastern Cape which, through carry-over into the rinse bowls by the wool, resulted in a deterioration of the dirty rinse water quality. Under normal conditions the carry-over of any water from the ponds would, however, be minimal.

During the first year of operation serious breakdowns were frequent and costs of maintenance, electricity and steam were very high. It was estimated that it cost some R16 to treat one kilolitre of water and recycle it to the plant. During the next year of operation there were significant improvements in the costs of maintenance, repairs and labour. Latest estimates, allowing for savings in municipal water and effluent handling and potential energy recovery, are that it costs approximately R 8,60 to treat one kilolitre of water and recycle it to the plant. This cost is , however, considered too high to be commercially viable at the present time.

1.4.4 Limited Trials with a Ceramic Substrate in a Low Pressure System

Limited trials with a ceramic substratum and zirconium oxide membrane indicated that high fluxes of reasonably good quality permeate may be possible at operating pressures of only 10% of that presently used in the stainless steel plant, but more work is required in this area.

1.5 REALISATION OF OBJECTIVES & CONTRIBUTION TO THE STATE OF THE ART

The project has clearly shown that dynamic ultrafiltration is a technically feasible technology for the treatment of both scouring effluent as well as dirty rinse water from the scouring operation. While the quality of the permeate from the scouring effluent was unacceptable for re-use in the factory's scouring operation as a partial replacement of Town's Water, the quality of the permeate from the dirty rinse water was satisfactory. Water recoveries of approximately 85% were achieved.

Limited recycle of permeate as a partial replacement of Town's Water had no detectable effect on the quality of the scoured wool product. This, coupled with integration of the firm's biological degradation ponds into the scouring loop, enabled a reduction of 50% on traditional Town's Water use for the scouring of raw wool. Recycle of water from the ponds for use in both the scouring and carbonising operations, has resulted in a 40% reduction in the consumption of soda-ash.

Maintenance, repairs and labour costs were very high during the first year of operation and although these have been significantly better during the second year, the running costs associated with the treatment and recycle of rinse water using a stainless steel substratum in a high pressure system are too high to be commercially viable at the present time. There is hope, however, that other similar technologies such as those employing ceramic membranes in a low pressure system may be more cost-effective.

The incorporation of an automatic membrane forming facility to facilitate the frequent stripping and reforming of the dynamic membranes proved to be extremely helpful and saved considerable labour costs. This facility could well find use in other industrial applications where fouling frequency is a problem.

1.6 RECOMMENDATIONS FOR FURTHER RESEARCH

It is recommended that further work be carried out on the use of dynamic membranes for the treatment of wool scouring effluent, more specifically on dirty rinse water which, by virtue of its superior quality when compared with that of waste water from the scouring bowls, can produce a permeate which can be readily re-used. Such research should be directed towards improving the economics of the system, and should preferably be concentrated on a low pressure technology. In this respect it is important that a thorough investigation be made into the potential of using ceramic membranes. Messrs. Gubb & Inggs fully intend to explore this path in the near future.

1.7 ACKNOWLEDGEMENTS

The research work pertaining to this publication was funded by the Water Research Commission under project number 161 entitled *Research into the Treatment of Wool Scouring Effluents*.

The Steering Committee responsible for this project in its final stages consisted of the following persons :

Dr O O Hart	Water Research Commission
Mr D Albertyn	Gubb & Inggs
Prof C A Buckley	University of Natal
Mr D J van Deemter	Gubb & Inggs
Prof F G Neytzell-de Wilde	University of Natal
Mr C H Steenkamp	Gubb & Inggs
Mr R B Townsend	University of Natal
Mr N Tegart	Steffen, Robertson & Kirsten
Dr D W F Turpie	Gubb & Inggs
Mr P W Weideman	Water Research Commission

Other persons who previously served on this Committee were as follows :

Mr L A Eichstadt	Dept of Water Affairs & Forestry
Dr T E Mozes	CSIR
Mr J Becker	SA Wool Board
Mr R J J Egenes	University of Natal
Dr R A Ollerman	CSIR
Mr J L Pretorius	Dept of Water Affairs & Forestry
Mr A B Lucas	Dept of Water Affairs & Forestry
Mr J A C Cowan	Binnie & Partners
Dr T C Erasmus	Water Research Commission
Dr C J Schutte	Water Research Commission
Mrs A E Simpson	University of Natal
Mr C J Brouckaert	University of Natal
Dr W H J Hattingh	Water Research Commission
Dr J v R Stander	Dept of Water Affairs
Mr I A Holman	Binnie & Partners
Mr T P M Young	Binnie & Partners
Prof J D Raal	University of Natal
Mr S Shlagman	Textile Federation
Mrs C Brazer	Textile Federation

In addition to the above, many of the staff at Gubb & Inggs and at the University of Natal made their facilities and time available.

The authors wish to record their sincere appreciation to all those who contributed to the Steering Committee and to all those persons who were involved in the execution and management of the project itself.

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ABBREVIATIONS

COD	-	chemical oxygen demand
USA	-	United States of America
UK	-	United Kingdom
BWK	-	Bremer Woll Kamerei, Germany
WRONZ	-	Wool Research Organisation of New Zealand
SS	-	suspended solids
TS	-	total solids
TDS	-	total suspended solids
WRC	-	Water Research Commission
IAWPRC	-	International Association for Water Pollution Research and Control
p.a.	-	per annum
SAWTRI	-	South African Wool and Textile Research Institute
UNSW	-	University of New South Wales
DSIR	-	Department of Scientific and Industrial Research, New Zealand
ICI	-	Imperial Chemical Industries, UK
MLSS	-	mixed liquor suspended solids
CSIRO	-	Commonwealth Scientific and Industrial Research Organisation, Australia
PCL	-	proteinaceous contaminant layer

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CHAPTER 1
INTRODUCTION

Before the raw wool of the sheep, or the raw hair of the angora goat (mohair) can be carded and spun into yarn on an industrial scale, it has to be cleansed (scoured) of its natural impurities, and when this is carried out in aqueous medium it leads to the production of an extraordinarily stable effluent which is both unsuitable for discharge to the environment and very difficult to deal with. In addition, a relatively large amount of water is normally required. Research into the treatment of such effluent, and extending also to water usage, has been carried out by laboratories and industries in many parts of the world, with varying degrees of success and cost-effectiveness, many applications being better suited to a particular set of circumstances than to others. It is on-going as newer, better or more viable technologies emerge, and as changes in environmental targets take place. The present report addresses the area of dynamic ultrafiltration as a potential contender of interest to the South African scene.

1.1 CONTAMINANTS OF THE FLEECE

The principal contaminants of the fleece are grease (the secretion of the sebaceous gland), suint (the water-soluble secretion of the sudoriferous gland), soil particles and vegetable matter (which attach themselves to the fleece in the pasture). There may also be significant quantities of adhering fecal matter.

The amount of impurity in the raw fibre can vary enormously, from as little as 14 % of fleece mass in the case of a *high-yielding* mohair, to as much as 65 % of the fleece mass in the case of a *low-yielding* wool. The wool grease is a highly complex mixture of oils and wax-like compounds (Truter, 1956), has a melting point of 35 to 40 °C, and a molecular weight of 790 to 880. Part of this grease is polar in character, and forms highly stable emulsions during scouring, and cannot be separated by centrifugal means. The remaining less-polar part can be dealt with centrifugally with reasonable success.

The suint consists mainly of potassium salts of fatty acids, urine, photodegradation products and colouring matter (Truter, 1956). It is an excellent medium for the culture of bacteria and fungi.

The dirt has a particle size distribution which varies greatly from wool to wool, in a range of about 1 to 400 μm (Mozes and Turpie, 1979).

1.2 REMOVAL OF IMPURITIES

In South Africa, as well as most other parts of the world, the natural impurities are removed by an aqueous washing process which is referred to as *scouring*, and this takes place in a series of from four to six *vats*, or scouring bowls, using hot water containing small amounts of a suitable detergent together, in the early stages, with small amounts of soda-ash. In some instances, cold water is used in the first bowl as a preliminary step. Where removal of all the residual vegetable matter is also desired, treatment with sulphuric acid follows scouring and the fibre is then dried, the vegetable matter baked, carbonised and crushed, and the fibre then de-dusted and neutralised with soda-ash in a further aqueous treatment. This process is referred to as *carbonising*.

1.3 POLLUTION LOAD

The wool scouring industry in South Africa produces a pollution load of approximately 8 Mkg of grease, 5 Mkg of suint and 12 Mkg of solids (Groves, 1979). It also utilises some 500 Mℓ of good quality water. At present only about half the clip is scoured in South Africa. Expansion of the industry is handicapped both here and in other producer countries (Australia and New Zealand) by the pollution problem, while at the same time there is an opportunity to increase market share as environmental pressures overseas tend to force the early processing stages back to the countries of origin.

1.4 CHARACTERISTICS OF THE EFFLUENT FROM WOOL SCOURING

During scouring, the grease is emulsified into the detergent solution, the suint dissolves, and the mineral particles become suspended. Even after a primary settling treatment followed by centrifugation aimed at the removal of the so-called *recoverable*, non-polar fraction of the grease together with the coarser suspended solids, an extraordinarily stable effluent remains, having characteristics, in the case of a wool scouring effluent, akin to those shown in Table 1.1 (Pearson et al., 1976).

1.5 RATIONALISATION

Effluents such as the above are highly polluting and necessitate treatment before disposal. The effluent load, as well as the fresh water consumption, can be significantly reduced by rationalisation of the scouring process to include a counter-flow of liquor through the bowls, liquor settling, sludge removal and dewatering, grease recovery, liquor recycle, evaporation and incineration (Gibson et al., 1981). Various systems are available - the choice depending on cost, legislation, local conditions, degree of treatment necessary and land availability.

TABLE 1.1 Characteristics of Wool Scouring Effluents (after Pearson et al., 1976)	
Grease	5 000 - 25 000
Detergent	100 - 1 000
Settlable solids	4 000 - 20 000
Total solids	10 000 - 80 000
Total dissolved solids	3 000 - 20 000
Biological oxygen demand	3 000 - 25 000
Chemical oxygen demand	5 000 - 150 000
pH	7 - 10

All determinands, except pH, in mg/ℓ.

1.6 EFFLUENT TREATMENT AND THE ENVIRONMENT

There is no doubt that environmental pollution throughout the world has become an important issue, and in many instances legislation has been invoked to improve the quality of the environment, and in particular, to prevent the pollution of local rivers (Robinson et al., 1980). Until recently the accepted method of textile effluent treatment, both in Europe and the USA, has been by conventional or extended aeration activated sludge plants, but many mills have discharged their effluent directly to stream with minimal pre-treatment. Now, the regulations are becoming increasingly stringent with limitations being set on, *inter alia*, biological oxygen demand (BOD), settlable solids (SS), chemical oxygen demand (COD), total solids (TS), total dissolved solids (TDS), pH, colour, oil, grease, chromium, sulphide and coliform. Stringent laws and consent limits have been set in Japan and elsewhere, necessitating high capital and running cost processes such as those involving concentration, evaporation and incineration. Such changes have resulted in a tendency for more and more scouring to take place in the grower countries, and for an increase in research and development effort in this field. Developments have included processes such as acid cracking, chemical flocculation, biological treatments, centrifugal treatments, solvent systems, ultrafiltration systems, evaporation and incineration, and low-liquor in-scour systems, such as the *Low-flo* and the WRONZ *Mini-bowl*. While each of these have found application in industry, none provide a complete solution to the treatment and disposal of effluent, and research continues.

1.7 PILOT PLANT WORK BY THE UNIVERSITY OF NATAL

The Water Research Commission supported a pilot-plant project by the Pollution Research Group of the University of Natal from 1980 to 1983 that developed a new treatment system for the above-mentioned effluent, including water re-use. This consisted of :

(i) desuinting/scouring,

(ii) evaporation of the desuinting effluent with water re-use and

(iii) dynamic ultrafiltration of the scouring effluent with water re-use

and it provided for about 90 % water re-use. Dynamic ultrafiltration appeared to provide the technology required for the treatment of such high-strength, fouling material and to play a role in the rejection of mineral salts - a feature of major importance to safeguard water quality, and to allow optimisation of the country's limited water resources. It was important that this pilot-plant work be followed up for the ultimate benefit of the industry and the environment.

1.8 MILL SELECTION AND AGREEMENT

In the case of Gubb & Inggs, the mill is one of the largest of its kind in the Southern Hemisphere, and is probably involved in scouring the widest selection of fibres, including wool, karakul and mohair fleeces, bellies, locks and mixtures of all kinds. The mill is situated in a rural area and is equipped with large tracts of land and evaporation and biodegradation ponds. Its selection as the site for further work, leading ultimately to full-scale trials, was therefore an obvious one. Accordingly, in 1985, an agreement was entered into between the Water Research Commission, the University of Natal (Pollution Research Group), Binnie & Partners (Consultants) and Gubb & Inggs, with the following objectives :

(i) to determine the technical feasibility of dynamic ultrafiltration in the treatment of *scouring* effluent for water re-use at high water recoveries.

(ii) to evaluate the reuse of the reclaimed water in the production environment.

(iii) to evaluate the processing performance and the cost effectiveness of the system.

(iv) to evaluate the mechanical performance of the system.

(v) to develop estimates of the net savings in water recycle, energy conservation, waste treatment and possible chemical recovery.

(vi) to develop a detailed design for the full-scale treatment of wool scouring effluents.

(vii) to progressively review the achievements of these objectives, and to ensure their successful completion.

Note : From 1st January 1986 Binnie & Partners amalgamated with Steffen Robertson & Kirsten and the new practice adopted the name Steffen Robertson & Kirsten.

1.9 SUBSEQUENT CHANGE IN DIRECTION

It will emerge from the results of the investigation pertaining to the above-mentioned contract, that while much useful data emerged, the system was not considered viable when conducted on *scouring* effluent. In 1990 it was agreed to suspend research in this direction and to change over to the treatment of dirty *rinse* water from the rinse bowls. At the same time it was agreed to integrate the firm's biological degradation ponds into the water and effluent loop. (See Chapter 5 for details).

CHAPTER 2
LITERATURE SURVEY

2.1 TREATMENT OF WOOL SCOURING EFFLUENT

The most recent survey of the wool scouring and effluent treatment situation, and developments throughout the world, was carried out by the International Wool Secretariat (Gibson et al., 1981). This discussed processes in current use as well as those in the process of development. A New Zealand perspective on raw wool scouring and an Australian perspective on developments in wool scouring were published by the International Wool Secretariat in 1987 (Stewart and Jamieson, 1987 and Christoe and Bateup, 1987). Collectively, the above-mentioned publications provide the most authoritative information on the global scouring and effluent treatment situation which is available, and all information provided below is taken from these sources unless otherwise stated.

2.1.1 Commercially Utilised Effluent Treatments

Table 2.1 summarises the effluent treatment processes in current use in 1979/80 and the level of COD reduction possible. The processes are usually applied after initial centrifugal grease recovery. Capital cost estimates are based on the cost to build new plant in the UK in 1979/80, over and above the grease recovery stage, and are also based on a scouring operation having a capacity of 5 000 tonnes per annum of greasy merino wool. Conversion to Rand costs in 1992/93 are based on an escalation rate of 10 % p.a. and an exchange rate of R5,3 = £1.

The data on acid cracking provided in Table 2.1 refers to batch treatment with sulphuric acid at pH 2 to 3. Traditionally, the equipment comprises tanks for cracking and settling, a magma boiler and filter presses to give grease. The process is labour intensive, and high in chemical cost, but generates some income from the acid cracked grease. The Idranova method uses acid cracking tanks and settling tanks, flocculation and sludge dewatering by rotary filter. It is labour intensive and higher in chemical cost, and no acid cracked grease is generated. The BWK method uses acid/bentonite for cracking/settling, filter-pressing cold and extraction of sludge with benzene to give grease which can be refined. COD reductions are generally over 80 %. Acid cracking is, however, associated with environmental pollution.

Chemical flocculation can be carried out at higher pH (e.g. 5 to 6), and COD reduction is superior to that of acid cracking. Capital costs are low. A relatively high level of inorganic salt (e.g. 0,5 to 1,0 %) is required to ensure effective cracking. In the Traflow process, ferrous sulphate and lime are used together with a rotary vacuum filter. An alternative is to flocculate with alum and ferric chloride or calcium chloride, preferably with a polyelectrolyte. This is followed by settling, sludge dewatering via a rotary vacuum filter or decanter. The process is expensive if a filter aid is used, but costs are lower with a decanter.

TABLE 2.1
Effluent Treatment Processes in Current Use (1979/80)

Type of Process	Method Equipment	Expected % COD Reduction	Capital cost Rand 1979/80#	Capital cost Rand 1992/93*
Acid Crack	Traditional Idranova BWK	80 to 85 80 to 85 80	135 000 135 000 270 000	1 248 000 1 248 000 2 495 000
Chem Floc	Traflow W Alum/Fe Cl_3	85 to 95 85 to 90	144 000 144 000	1 331 000 1 331 000
Biological	Lagooning/ irrigation	97	216 000	1 996 000
Centrifuge/ Evaporation	ITF/Alfa Laval or Dewavrin	100	756 000	6 986 000
Ultrafiltration/ Evaporation	Dorr-Oliver IOPOR or IOPLATES	80 to 85	360 000	3 327 000
Evaporation/ Incineration	Evap. to 30 to 40%, sludge drying and incineration	100	540 000	4 990 000

\# Based on exchange rate R1,8 = £1.

* Based on 10 % p.a. escalation, and exchange rate R5,3 = £1.

If a mill is situated in a rural area and has land available, the well-proven biological process, involving anaerobic/aerobic lagooning followed by spray irrigation, is not too expensive to install and produces an excellent COD reduction. Running costs were estimated to be R36 000 p.a. in 1979/80 (R333 000 p.a. in 1992/93). The process may not, however, be able to comply with local environmental requirements.

Centrifugal removal of grease followed by evaporation of the degreased effluent, as in the ITF/Alfa Laval of Dewavrin processes provides condensed water for reuse and a sludge which can be disposed to land. 100 % of the COD was removed. Capital costs are very high. Running costs were estimated to be R252 000 p.a. in 1979/80 (R2 329 000 p.a. in 1992/93).

Treatment by means of ultrafiltration/evaporation was still in its infancy at this time, and major commercial developments in ultrafiltration were confined mainly to Dorr Oliver and Abcor and to effluent from the scouring of carpet wools. The process produced an ultrafiltrate and a concentrate, and the latter was further concentrated in an evaporator. COD reductions of over 80 % were obtained. The process was associated with high capital and running costs, the latter being estimated to be in the region of R180 000 p.a. in 1979/80 (R1 663 000 in 1992/93).

Evaporation/incineration is essentially a zero discharge process in that the only product is an ash which could be valuable as a fertiliser. The treatment at this time was mainly confined to Japan and was associated with high capital and running costs, the latter being estimated at 6,5 c/kg raw wool in 1979/80 (R0,60/kg in 1992/93).

2.1.2 Effluent Treatments at Pilot or Semi-industrial Stage (1979/80)

Table 2.2 summarises the new processes which were developed in the five years prior to the IWS survey, but which were not at the stage fully proven under full-scale industrial conditions.

Hot acid flocculation is a development from the University of New South Wales (McCracken et al., 1977) and is essentially a closed process with odour problems reduced to a minimum. It is a continuous process, as opposed to earlier batch treatment processes, and operates at a pH of 2,5 to 3,0. Cracking takes place in a reactor and is followed by neutralisation, flocculation and sedimentation, and continuous sludge dewatering via a decanter centrifuge. Cracking is both efficient and rapid, giving a high solids sludge for disposal to land. COD removal is over 85 %. Capital cost is relatively low and the process lends itself to automatic monitoring and control. It has been tested at pilot level in Australian mills. Running costs are expected to be fairly low provided the high-solids sludge can be disposed to land cheaply.

Destabilisation of scour effluent by the magnesium-rich waste residue from a sea-water salt recovery plant (*bitterns*) developed by SAWTRI involves a relatively low capital cost, and running costs are low provided the plant is situated near the salt recovery plant (Mozes and Turpie, 1980). Grease removals of 80 to 95 % and COD reductions of about 95 % have been obtained using 5 to 6 % v/v of *bitterns* solution having a TS content of about 45 %. The scheme has not been tested commercially.

TABLE 2.2 New Processes at Pilot or Semi-industrial Level (1979/80)				
Type of Process	**Method Equipment**	**Expected % COD Reduction**	**Capital cost Rand 1979/80#**	**Capital cost Rand 1992/93***
Acid Crack	UNSW Hot Acid	85	180 000	1 663 000
Chem Floc	SAWTRI "Bitterns"	95	144 000	1 331 000
Biological	ICI Deep Shaft UNSW "Unisas"	99,7 98 to 99	450 000 144 000	4 158 000 1 331 000
Solvent	Provost Process (40 000 T p.a. plant) DSIR Alcohol	95 75	8 100 000 243 000	75 000 000 2 246 000
Ultrafiltration/ Evaporation	University of Natal	Unknown	180 000	1 663 000
# Based on exchange rate R1,8 = £1.				
* Based on 10 % p.a. escalation, and exchange rate R5,3 = £1.				

The ICI Deep Shaft process (ICI, 1977) is a high rate biological process in which effluent passes down a deep shaft with air/oxygen injection giving rapid oxygen transfer and rapid biological degradation. It has the advantage of almost total COD removal at low running costs and with low area requirement, but the disadvantage of high capital cost and restrictions of disposal of large quantities of voluminous sludge. The latter could be significantly reduced by employment of a decanter.

Another high rate biological development comes from the University of New South Wales and is known as the Unisas Superactivated sludge process (Chaikin and McCracken, 1977) which was designed to work on high strength wastes. The process is an automated, technologically up-dated variation of the conventional activated sludge process, but the plant is much smaller than for other conventional biological treatments. Optimum temperature is 35 °C, the process is exothermic and runs with high MLSS and high biomass concentrations. Efficient oxygen transfer takes place with rapid biological breakdown (assuming the addition of nutrients) to obtain a correct balance of organic material to microorganisms and keep a healthy biomass. The plant does not suffer badly from poisoning or shock loads that can plague conventional activated sludge processes, and the plant can be shut down and started at will. The process is low in both capital and running costs and achieves a very high COD reduction. The quality of the effluent is expected to be about 1 000 mg/ℓ COD i.e. a COD reduction of over 98 %. The principle has been proven but not yet commercially exploited.

The Provost process is a patented solvent process in which the waste water is treated with perchlorethylene, centrifuged, clarified and distilled to give a grease-rich emulsion and a condensate from which the solvent is recovered. The process enables greasy matter, soil and dissolved salts to be separated, and produces completely degreased water with no suspended solids. The dirt can be recovered in anyhdrous form for disposing at little or no cost, or even sold as fertiliser. The process has been tested at pilot scale. Capital cost of a full-scale plant is expected to be extremely high. Running costs were estimated to be 2,7 c/kg greasy in 1979/80 (R0,25/kg in 1992/93).

The DSIR solvent process (Smith & McLachlan) uses the principle of solvent destabilisation with n-pentanol and a polyelectrolyte to give a grease rich top solvent phase, a middle phase containing essentially suint liquor and a bottom dirt phase. The three streams are then evaporated on packed columns to separate the constituents. Performance of the plant was expected to give a COD reduction of 75 % and a grease yield of 80 %. Running costs were expected to be relatively high since not only is it a solvent process, but it also involves steam distillation.

The University of Natal ultrafiltration process was originally described as in *in-scour* scheme in which desuinting took place in the first bowl using a low-volume flow (1 to 2 ℓ/kg wool) which was then evaporated. The evaporator condensate was recycled to the rinse bowl. Discharge from the scouring bowls was passed through a dynamic membrane porous stainless steel tubular ultrafiltration system to separate grease and dirt from the water. The ultrafiltrate was recycled back to the scour. No information was provided on whether grease could be recovered from the concentrate, nor what the running costs were likely to be.

2.2 RELEVANT MEMBRANE TECHNOLOGY

2.2.1 Application of Membranes

Following the development of efficient, anisotropic, semi-permeable membranes in the 1960's an effective tool for the fractionation, concentration and purification of macromolecules in solution, and colloids in suspension, was gained (Messinger et al., 1975). One of the main initial applications was desalination, but more recently the technology has been used for the treatment of a variety of industrial effluents for pollution abatement and water re-use. During the 1970's the CSIRO examined the application of ultrafiltration membrane separation technology as a possible means of producing a clear wastewater from wool scouring effluent which had been centrifugally treated (Pearson et al., 1976). Fouling or *blinding* of the membranes, with resultant flux decline, proved to be a serious problem, although it was claimed that flux rates could be restored by various cleaning procedures. Membrane life, however, was assumed to be about one year.

2.2.2 Dynamic Membranes

Incompatibility of the membrane with the chemical nature, temperature, and solids content of the effluent often limit the selection of the membranes available, have an important bearing on the life of the membrane, and may make the use of extensive pre-treatment of the effluent essential and expensive. The use of dynamic or *formed-in-place* membranes pioneered by the Oak Ridge National Laboratory (Marcinkowsky, et al., 1966 and Johnson et al., 1972) appeared to offer certain advantages in so far as :

(i) they could be formed on a robust support tube having a long service life.

(ii) they could be operated at high pressure and temperatures.

(iii) when fouled they could be removed by chemical means and be re-formed *in situ*.

(iv) pre-treatment to remove solids was not a prerequisite.

Research indicated that membranes of the hydrous zirconium (iv) oxide type were more suitable than many other hydrous oxides which were tested. Nevertheless, no information was available on the possible application of this technology to the wool and mohair scouring industry.

2.2.3 Formation of Dynamic Zirconium Membranes

Zirconium type membranes are formed by the deposition of hydrous zirconium (iv) oxide onto the porous structure of a suitable support from colloidal suspensions. Stringently controlled conditions are necessary for the formation of high performance membranes.

Since stable zirconium chelate complexes form with many organic compounds by co-ordination through oxygen atoms, this enables the deposition of certain polymers onto the hydrous zirconium (iv) oxide membrane layer. This in turn then leads to the possibility of tailoring a membrane for specific duties.

The methods of formation are described in detail by Johnson et al. (1972). It has been proposed by Freilich and Tanny (1978) and Tanny and Johnson (1978) that when a dilute colloidal suspension of hydrous zirconium (iv) oxide, at a pH just below 4, is passed across the surface of a porous substrate, the first stage involves a pore-filling, or bridging stage, where colloidal particles of hydrous zirconium (iv) oxide are captured on the walls of the porous support material. This process causes the pores to close after a period and is followed by formation of a surface filtrate cake from colloidal particles, as commonly occurs in other types of cross-flow microfiltration. This then represents the hydrous zirconium (iv) membrane which, in acidic solutions, is an anion exchanger.

The hydrous zirconium (iv) oxide membranes are characterised by high water fluxes (150 $\ell/m^2h.MPa$) whilst showing a significant salt rejection (40 %).

To distinguish these membranes from conventional phase inversion membrane films prepared by casting or other means, the class is designated *dynamically formed* or *dynamic*. More recently they have been referred to as *formed-in-place* membranes.

2.2.4 Stainless Steel Supports for Dynamic Membranes

Most of the early research was conducted using porous carbon or ceramic support tubes, but problems with the robustness of the tubes limited the applicability of the research. Brandon et al. (1980) and Mott et al. (1977) used porous stainless steel as a support for dynamic membranes which overcame most of the problems associated with the carbon and ceramic tubes. Carre Inc. (1982) referred to the reliability of porous sintered stainless steel as the support material for high temperature dynamic membranes. Because of the integrity of the material, high-pressure operation is possible and single pass tubular dynamic membrane systems were developed. Also, because the dynamic membrane is replaceable, fouling considerations are minimised and high strength industrial effluents may often be treated successfully.

CHAPTER 3
WOOL SCOURING, AND THE SCOURING MACHINE USED IN THIS WORK

3.1 WOOL SCOURING (Christoe and Bateup, 1987)

3.1.1 Mechanism and Theory

In the past, raw wool was considered to contain three main scouring contaminants - wool grease, suint and dirt. When the wool was scoured, the grease was emulsified, the suint was dissolved and the dirt was suspended in the scouring liquor. Scouring was seen as a three-stage process :

(i) The raw wool was wet out, its temperature was raised above the melting point of the wool grease, and the detergent molecules, needed for scouring, were brought up to the fibre by liquor flow and diffusion;

(ii) Formation of surface films of detergent molecules, rolling up of the grease into droplets and sweeping them into solution by an adequate flow of liquor.

(iii) Removal of excess detergent and builder by rinsing.

Unfortunately this simple picture did not explain a number of anomalous situations which included :

(i) Wool grease on the tips of fibres is harder to remove than grease from the base;

(ii) Similar scouring systems remove the contaminants from wool to different extents;

(iii) Large quantities of rinse water are needed to improve wool colour;

(iv) Only about 50 % of wool grease is recoverable by centrifuging;

(v) Dirt recovery from scouring liquors varies considerably;

(vi) In rinsing bowls voluminous grey sludges are often encountered;

(vii) Scouring effluents are unusually difficult to acid-crack or flocculate.

A major breakthrough in scouring theory came from the demonstration that wool grease is comprised of two fractions - an oxidised fraction that is found mainly at the tip and an unoxidised fraction that is purest at the base of the fibre. During scouring the unoxidised fraction is more readily removed and recovered by centrifuging whereas the oxidised fraction forms complexes with other contaminants in the scouring liquor and is unrecoverable by centrifuging under the conditions existing in a commercial centrifuge.

Further significant developments in scouring theory occurred in the late 1970's when, as a result of fundamental studies, a fourth major raw-wool contaminant was identified. This was named the proteinaceous contaminant layer (PCL). Subsequent work showed that these proteinaceous contaminants comprised mainly skin flakes and soluble peptides, and the PCL was used to explain some of the anomalous effects referred to above.

More recently it was shown that all the contaminants, not only wool grease, could be divided into two fractions - an easy-to-remove fraction and a hard-to-remove fraction. The former comprises the unoxidised grease, most of the oxidised, readily-soluble suint and loosely held mineral, organic and proteinaceous dirt. The latter comprises a small fraction of the total oxidised grease, slowly-soluble suint, sub-micron mineral dirt and flakes of proteinaceous contaminants adhering to the fibre surface.

The current picture of contaminant removal from raw wool is as follows :

(i) Penetration of the grease by water and surfactant followed by rapid swelling of both grease and proteinaceous contaminants (some solubilisation of oxidised grease within surface micelles may also occur);

(ii) Formation of grease globules (unoxidised in particular) within the swollen mass;

(iii) Removal of the complexed and uncomplexed easy-to-remove contaminants which are not strongly bound to the fibre surface;

(iv) Partial removal of the hard-to-remove contaminants such as swollen proteinaceous contaminants adhering to the fibre surface along with complexed grease and suint.

3.1.2 Equipment

In the 1940's a typical wool scouring line consisted of four bowls that were constructed of cast iron, were four feet (1,2 m) wide, had overhead harrows, had squeeze rollers lapped with crossbred-wool top, and were thirty feet long with an irregular cross section which allowed solids to accumulate towards the side. The scouring line was arranged so that the bowls were at the level of the operator - the piping was below floor level.

Although the basic principles involved in scouring, namely wetting out of the wool, conveying the wool through the bowl and transferring the wool to a squeeze roller set, have not changed, there have been subtle changes in the design of a scouring set.

A modern scour, which is constructed of stainless steel, consists of more bowls (five or six) that are shorter in length but wider and above floor level. The wool is wetted out using rotary dunkers. Rakes or harrows are used to propel the wool through each bowl. The former is preferred because the fitting of bowl covers for energy conservation is simpler. The top squeezing rollers are covered with a plaited square rope made from a synthetic fibre or a synthetic fibre/wool blend. These ropes have a significantly longer operating life which justifies the higher initial cost. Scouring production rates are considerably higher.

3.1.3 Bowl Functions

A scouring bowl can perform one of three functions - desuinting, scouring or rinsing. A desuint bowl (cold water; placed first in the scouring train) removes most of the water-soluble contaminants as well as some of the more loosely adhering dirt. The amount of dirt removed depends strongly on the characteristics of the greasy wool. A scouring bowl (hot water), which contains a detergent and possibly a detergent builder, removes contaminants from the fibre by classical detergency mechanisms. A rinsing bowl (warm water) removes the contaminants in the scouring liquor entrained in the wool, along with some particulate matter loosely adhering to the wool.

The conventional configuration of a scouring train is to have two or three scouring bowls followed by two or three rinsing bowls (in some cases the first bowl is used as a desuinting bowl). More recent configurations are those of two-stage scouring, which includes an intermediate rinsing stage between the first and second scouring bowls, and three-stage scouring which, in addition, utilises a desuinting bowl that contains a small amount of detergent and alkaline builder prior to the first scouring bowl.

3.1.4 Bowl Design

In an ideal scouring system using counter-current flow, scouring should continue indefinitely providing that the flow of water and the contaminant recovery systems are sufficient to keep the levels of contaminants in the bowls at sufficiently low levels. Unfortunately contaminants, dirt in particular, accumulate in the bowls until scouring must be stopped, the liquors dropped and the bowls cleaned.

Older types of scouring bowl consisted of a rectangular tank assembled in sections. Each section had a 30 to 60 degree hopper bottom with a discharge valve at the bottom. These values were opened periodically to discharge accumulated sludge. These discharge valves blocked with dirt with monotonous regularity and the self-cleaning bowl, having a bottom section of triangular shape, was designed to encourage settling onto a screw conveyor which transferred the sediment to a central discharge port. However, in both the above systems, considerable amount of scouring liquor containing recoverable wool grease, usable detergent and heat were lost. Modern systems employ a high rate of flow of liquor from the scouring bowls to the contaminant recovery system, and the rate of accumulation of dirt in the bowls is significantly reduced.

3.1.5 Contaminant Recovery Loops

An important component of a wool scouring plant is an effective contaminant removal and recovery system - effective removal because it enables the scour to operate more productively and effective recovery because it reduces the discharge of contaminants to the external environment.

The trend in industry today has been to buy a scouring package that consists not only of the scouring line itself, but also a contaminant and recovery section. The WRONZ Comprehensive Scouring System represents the first system that seriously offered a complete package. The Lo-Flo System and Mini-flo (the IWS-developed combination of the WRONZ and Lo-Flo systems), also offered a complete package. More recently SIROSCOUR emerged as an optimised scouring and contaminant recovery package developed by CSIRO in Australia.

3.1.6 Factors Involved in Contaminant Removal

Detergents : Before the 1950's virtually the only detergent used to scour wool was soap which was used with an alkaline builder, usually soda ash. Synthetic non-ionic detergents were introduced to the scouring industry firstly in the USA. Because of their ease of use and cost effectiveness, they have displaced soap as the principle detergent used in scouring. Although questions were raised about their biodegradability, and price rises due to the oil crises in the 1970's caused some problems with their use, they continue to be the most commonly used.

The optimum way of using a detergent in the scouring line depends on a number of factors which include the type of wool being scoured, the method of addition, the number of bowls in the scouring train, the bowl configuration and the flow of liquor through the bowls.

Wools containing high levels of wool grease and low levels of suint require considerably more detergent than wools containing low levels of grease and high levels of suint. For example, typical Australian merino wools need about 0,6 % to 1,0 % detergent on the weight of raw wool, whereas New Zealand crossbred fleeces only require 0,1 % to 0,2 %. Continuous addition has been shown to be more efficient than discontinuous addition. Also, the role of suint as a detergent in its own right should not be neglected, especially with crossbred wools in which the suint is usually alkaline.

Builders : Virtually the only builder now in use is soda ash. It is usually added either in the first scouring bowl to improve contaminant removal, or in the final rinse bowl to improve subsequent processing performance.

Temperature : In soap/soda scouring the scouring temperature is less than 55 °C because of the possibility of alkaline damage to the wool at higher temperatures. With non-ionic detergents higher temperatures of about 60 to 65 °C are usually used. Although the efficiency of grease removal increases with temperature the bowl temperatures should be kept below 70 °C to reduce wool damage and limit energy wastage. Rinsing temperatures should be warm rather than cold to reduce residual moisture on the scoured wool before drying, thereby reducing the drying cost and overall energy usage.

Water quality : There are two sorts of problems associated with water quality. These are hardness and the presence of multivalent metal ions. In the past the water used in scouring had to be very soft because of the tendency of calcium and magnesium to precipitate as soap. With non-ionic detergents this problem is not as severe. However, their presence in the scouring liquor could cause both redeposition of fibre contaminants and dyeing problems. Apart from the cations mentioned above, the presence of metal ions such as iron can cause severe dyeing problems by interacting with dyestuffs.

3.2 WATER USE (Gibson, Morgan & Robinson, 1981)

Water use depends on a number of factors such as the degree of rationalisation of the scouring process and liquor handling systems and the type and quality of the wool being scoured.

Traditionally, using a basic design of scouring machine in which all the pollutants on the wool are periodically dropped to drain, a relatively clean merino wool of 22 μm diameter normally utilises some 10 ℓ of fresh water per kg of raw material. At a production rate of 1 000 kg greasy wool per hour some 120 kg grease, 80 kg suint and 80 kg dirt would be removed per hour, producing a COD load of 474 kg/hour, or approximately 50 000 mg/ℓ.

By including a settler and centrifuges in the above system, and introducing a counter-flow of liquor from clean bowls to the dirtier bowls, a regular discharge of effluent can be obtained and the pollution load can be reduced by about one third by removing about 30 % of the grease in a one-pass system.

In more modern technologies such as the WRONZ rationalised system (forerunner of the mini-bowl scouring technology of today), which incorporates a flock catcher, heavy solids settling tank, heat exchangers and grease plant, and in which most of the liquor is recycled back to the scour, water consumption can be reduced to 3,5 ℓ/kg grease wool, and the COD load can be reduced by 47 %. In such a system grease recovery is about 43 %.

3.3 THE SCOURING MACHINE USED IN THIS WORK

One of the washlines at the factory of Gubb & Inggs, Uitenhage, known as *Washline 4* was dedicated to this project. A schematic diagram of Washline 4 is shown in Figure 3.1. The essential elements of the washline were as follows :

TABLE 3.1
Washline No.4 Dimensions and Capacity

	Approximate length (m)	Approximate capacity (ℓ)
Feed lattice, hopper and weightbelt	12	
Greasy wool opener	3	
Washbowl No. 1	8	10 000
Washbowl No. 2	8	10 000
Washbowl No. 3	5	5 000
Washbowl No. 4	5	5 000
Washbowl No. 5	5	5 000
Hot air Dryer	12	
TOTAL	58	35 000

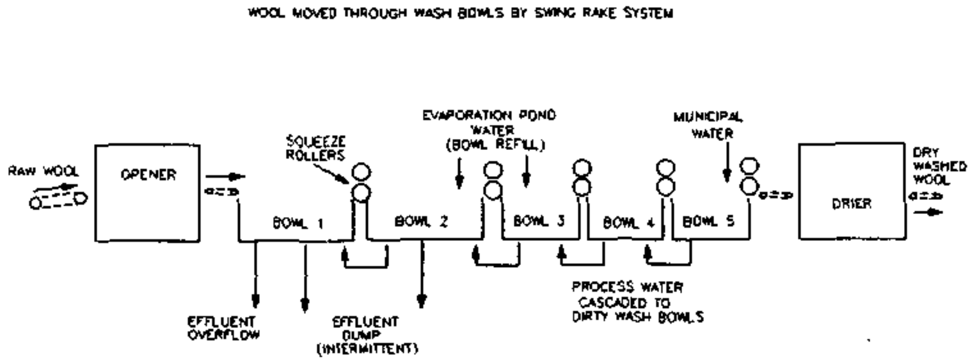

FIGURE 3.1 : Schematic Diagram of Washline No. 4

The level of the floor can be seen from the base of the feed hopper. The washbowls were filled with water to a height very close to their maximum dimension. Removable close-fitting grids were fitted to each bowl between the water level and the floor level as shown, their purpose being to contain the wool while at the same time allowing the suspended matter to pass through. All the bowls had tapered bottoms for facilitation of sludge collection, extending well below the level of the floor.

The raw wool emerging from the opener was first dunked under the water level in bowl 1 to wet it out, then lifted up and down while at the same time being propelled in the water along the length of the bowl by means of a *swing-rake* overhead drive mechanism (not shown in figure). At the end of the bowl the wet wool was raised from the level of the liquor to a sufficiently high level by means of a device known as the *Belgian lift* (not shown) to enable it to be fed into the nip of a pair of heavy duty squeeze rollers positioned at the end of the washbowl. At this point all excess liquor, and a relatively large amount of associated contaminants, were squeezed from the wool, and the squeezed product then passed into the next wash bowl. No dunking mechanism was used on subsequent bowls, but in all other respects the same procedure was followed until the wool emerged from the fifth washbowl. At this point it entered the dryer, finally emerging as a commercial scoured product.

For the entire duration of the project raw wools of widely different character were scoured on this washline, from high-yielding fleeces to low-yield outsorts, according to production demands at the time. These demands were in no way influenced by the fact that a research project was being undertaken simultaneously.

The reticulation systems used in the project were specific to the research mode, i.e. whether the ultrafiltration plant was being used for the purification of water from the *scouring* bowls or the *rinse* bowls. Details are given in Chapters 4 and 5.

CHAPTER 4
THE MODULAR DEMONSTRATION PLANT, AND RESEARCH ON EFFLUENT FROM THE SCOURING BOWLS

4.1 THE MODULAR DEMONSTRATION PLANT

A modular demonstration ultrafiltration plant was constructed at the factory, and was sited outside, a short distance away from the scouring plant, on a reinforced concrete pad. The essential elements of the plant were a large rectangular tank with conical bottom for receiving the desuint liquor and another similar tank for receiving the scouring liquor (or the rinsing liquor) from Washline 4; a batch pre-treatment tank in which a quantity of scouring liquor (or rinsing liquor) could be heated prior to membrane treatment; a batch treatment tank in which a specific batch of effluent could be concentrated by ultrafiltration; ten individual permeate trays each containing one dynamic membrane module; various pumps, valves, reticulation, and electronic controls.

Each dynamic membrane module was 3,5 m long and 215 mm in diameter and contained 150 m of 144 mm ID porous stainless tubes, having a total porous area of 6,38 m^2.

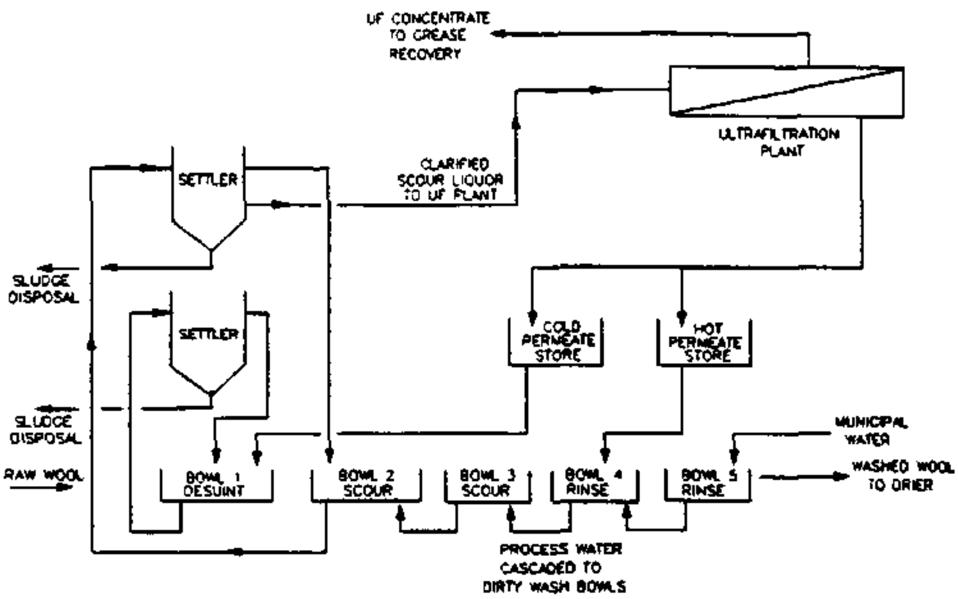

FIGURE 4.1 : Simplified Schematic of the Desuint-scour Effluent Treatment Process Showing only Main Process Flows

4.2 RESEARCH ON EFFLUENT FROM THE SCOURING BOWLS

4.2.1 Laboratory-scale/Pilot-plant Trials

Laboratory-scale experiments and subsequent pilot-plant trials at Gubb & Inggs Ltd indicated that dynamic membranes of the hydrous zirconium (iv) oxide type could be used successfully to treat the grease effluent. The permeate which was recycled was 85 % of the original feed. The membrane system was capable of rejecting 92 to 96 % of total organic carbon, and 85 to 90 % of the total solids. Grease rejection was 100 %. A plot of flux versus water recovery is shown in Figure 4.2.

4.2.2 Dynamic Ultrafiltration of Liquor from the Scouring Bowls

As a consequence of the pilot plant results the modular demonstration plant was constructed (see above), and this was operated for a period of approximately 12 months as a factory production unit.

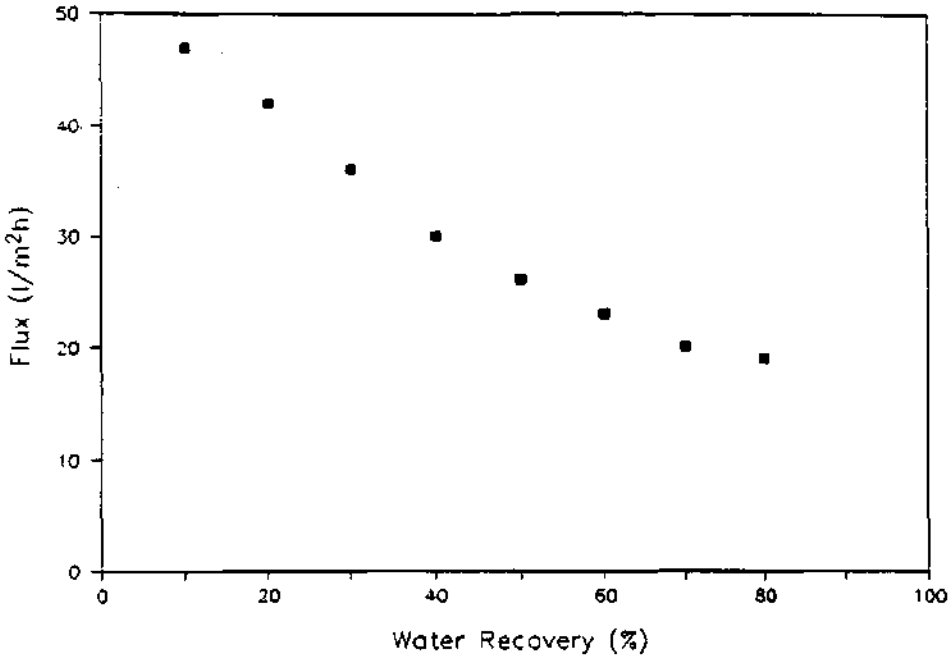

FIGURE 4.2 : Wool Scour Effluent. The Effect of Water Recovery on Permeate Flux

During the operating period the need for membrane re-formation was demonstrated as the modules became progressively fouled. In order to maintain the design flux the membranes were reformed on a two monthly cycle. Re-membraning was accomplished by chemically cleaning the fouled membranes to a bare tube state, and reforming the membrane.

At the end of the 12-months operation, 1 920 tons of raw wool had been processed, producing 1,7 Mℓ of scour effluent which was processed by the demonstration plant. During the plant operation, performance was monitored, and these results are presented below.

Overall Plant Permeate Flux : The overall permeate flux from the plant is shown in Figure 4.3.

Because the flux was dependent on the applied pressure, and the pressures were difficult to control, the flux measurements have been presented as a specific flux, i.e. $\ell/m^2h.MPa$. In addition, flux varied with total solids content of the feed, and in order to compare the measured flux with the predicted design flux, the predicted design flux for the solids content (in g/ℓ) at the time of measurement is included in Figure 4.3. The previously established relationship (Simpson and Groves, 1983) between permeate flux (J) and total solids (TS) content at an applied pressure of 5 MPa is :

$$J = 37 - 0.18\ TS$$

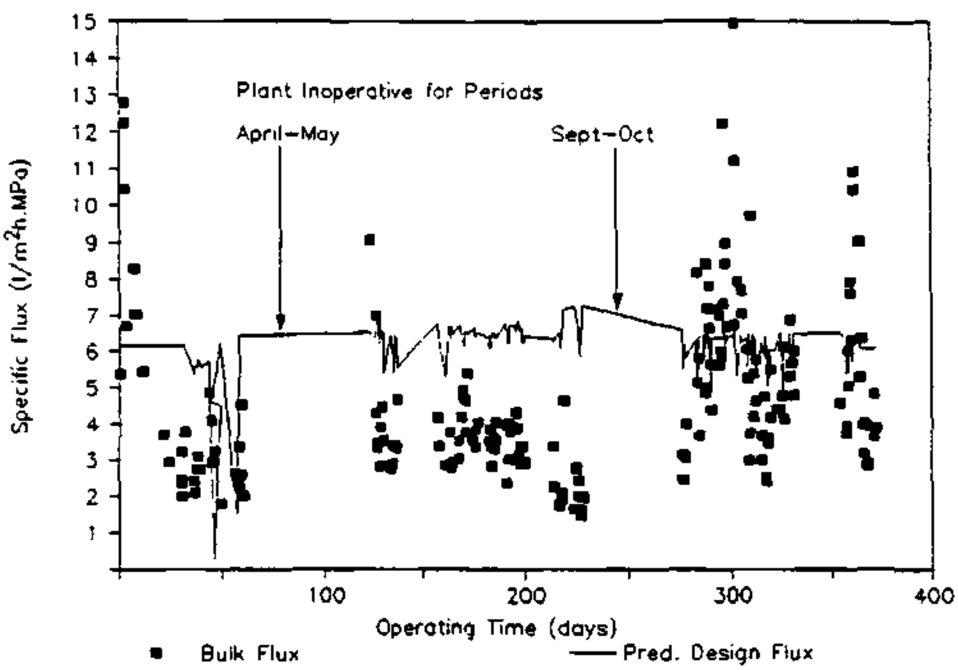

FIGURE 4.3 : Wool Scour Demonstration Plant Performance

It can be seen that, in the latter period of operation (280 d), after introduction of on-site membrane re-formation, there was a scatter of flux measurements about the predicted design flux, whereas previously the flux was below the design flux due to there being no facilities for on-site membrane formation, and hence the plant was operated for extended periods with fouled membranes.

Effect of Discontinuous Operation : It was found that the design flux could be maintained, provided that the plant operation was continuous. The results of a specific module are presented and compared to the design average flux (Figure 4.4). During the period from mid-November 1988 to early December 1988, the plant was subjected to numerous unscheduled stoppages. The effects of this were marked and are illustrated in Figure 4.4. Several days of operation were required before the flux was restored to its design value. It was concluded that any occurrence which resulted in the scour liquor cooling in the modules would result in module fouling.

Effect of Cross-flow Velocity on Flux : The module configuration comprised 10 modules in parallel, fed by two pumps operating in parallel. With both pumps in operation the tube velocity was 2 m/s; with one pump in operation the velocity was 1 m/s. Previous work on the wool scouring plant as well as laboratory work on synthetic polyvinyl alcohol solutions, indicated that a minimum velocity of 1,5 m/s was required to prevent gel layer polarisation which caused a reduction in permeate flux. While no detailed experiments were conducted on the demonstration plant in this regard, a failure of one of the two feed pumps presented a period of impromptu tests on low velocity performance. The adverse effect of flux is shown in Figure 4.5. Subsequent return to higher velocity operation did not restore the flux to the design value within a reasonable time span.

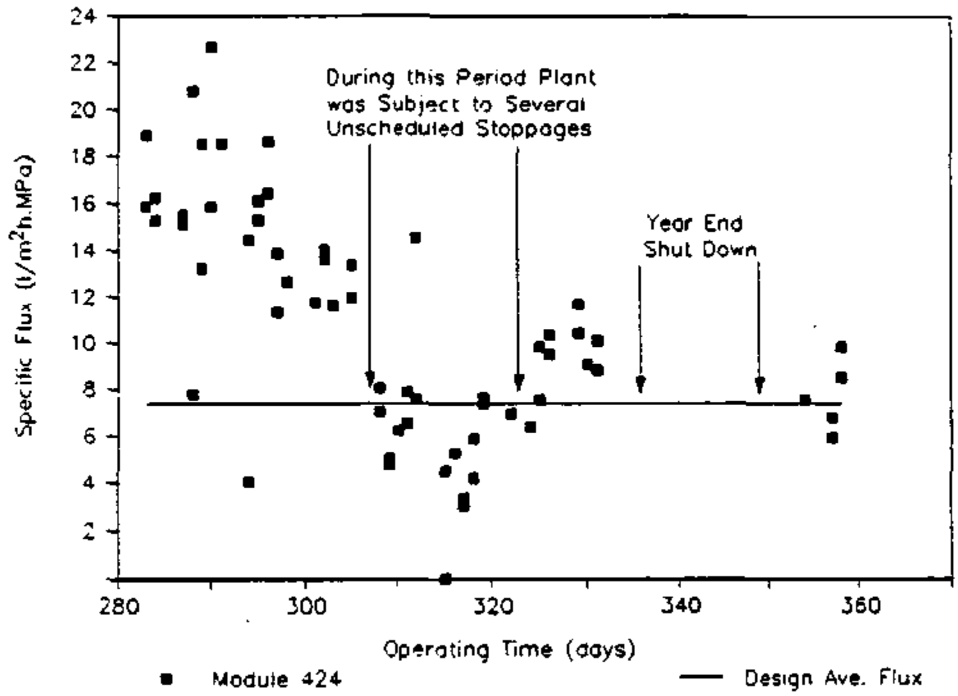

FIGURE 4.4 : Wool Scour Demonstration Plant. Effect of Intermittent Operation

Module Cleaning and Membrane Formation : The effect on a fouled module of chemical cleaning, membrane stripping and subsequent membrane re-formation is shown in Figure 4.6. Removal of the foulants and membrane stripping was accomplished by circulating approximately one-molar solutions of sodium hydroxide, sodium hydroxide/hydrogen peroxide mixture, and nitric acid, in turn, through the module.

This cleaning technique was carried out at 80 °C. It can be seen that restoration of the flux to that of a clean tube coated with a hydrous zirconium (iv) oxide membrane was possible.

Trials were also conducted on membrane cleaning techniques, without membrane re-formation. High temperature (80 °C) and high strength sodium hydroxide (pH 13) proved effective in removing grease from the membrane surface; however, the permeate flux was not significantly improved. This implied that the foulant was embedded or chemically bonded in the matrix of the membrane/substrate and significant flux restoration would not be possible without an alkali wash followed by an acid wash, and subsequent membrane re-formation.

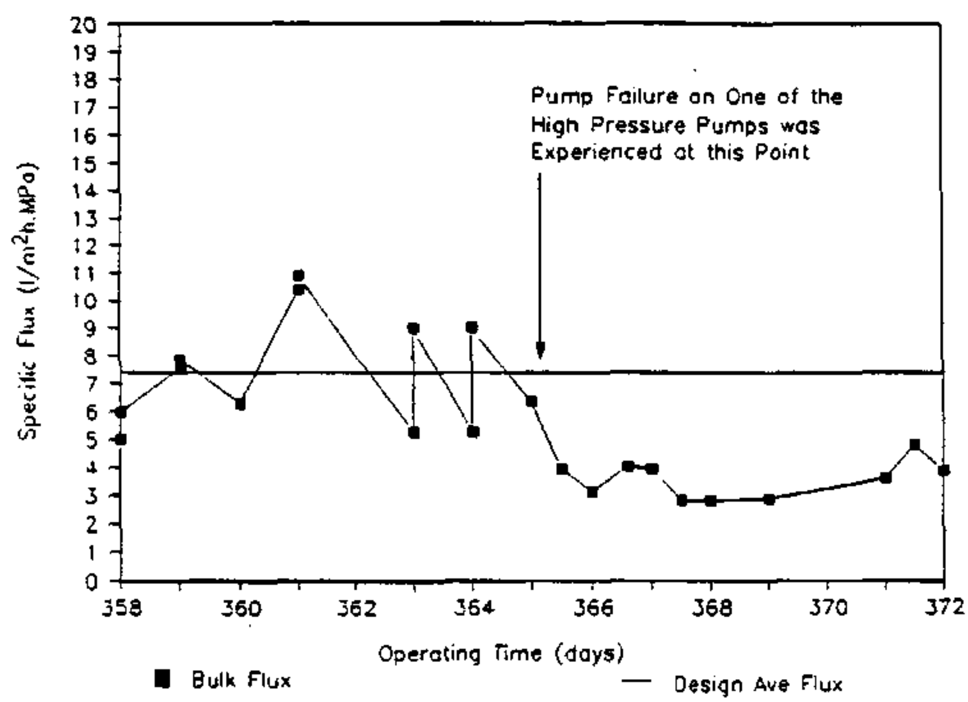

FIGURE 4.5 : Wool Scour Demonstration Plant. Effect of Low Cross-flow Velocity on Flux

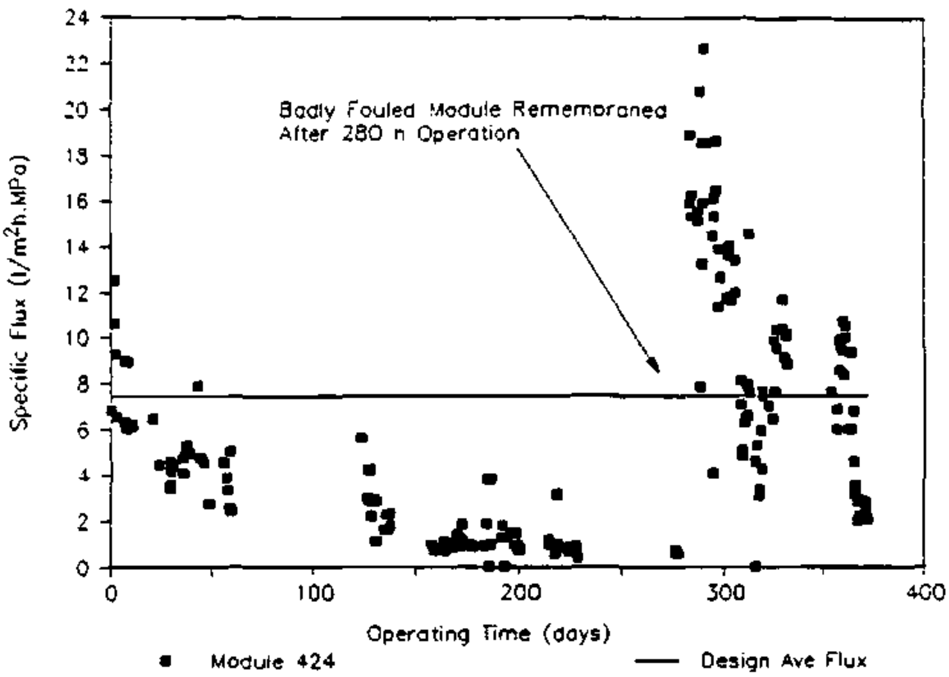

FIGURE 4.6 : Wool Scour Demonstration Plant. Effect of Membrane Reformation

Quality of the Permeate : Unfortunately the quality of the permeate was at all times too poor to be acceptable by management for re-use in the rinsing of the scoured wool product.

CHAPTER 5
CHANGE IN PHILOSOPHY AND INITIAL RESEARCH ON EFFLUENT FROM THE RINSE BOWLS

5.1 PHILOSOPHY BEHIND THE CHANGE TO RINSE WATER TREATMENT

It is an accepted fact that whatever the system of liquor handling and effluent treatment is selected in a commercial scouring operation, an adequate supply of relatively clean *rinse* water is necessary in order to produce a wool or mohair product of acceptable colour, odour and residual impurity content. This is extremely important.

One the other hand, the earlier stage of scouring can be - and generally are - carried out with water containing relatively high loads of wool contaminants, and with relatively small volumes.

It is clear, therefore, that an opportunity exists to reduce *fresh* water consumption dramatically, by purifying and recycling some of the *dirty rinse water* and reusing it for *rinsing*. This is particularly important in areas where water is scarce.

Because of the unacceptable quality of the permeate from wool scouring referred to above, and because of economic considerations e.g. a tertiary treatment plant would have to be installed, it was decided by the Steering Committee and endorsed by the Water Research Commission, to conduct trials on the treatment of effluent from the rinse bowls, since this looked, at first sight, to be an interesting alternative approach. At the same time the Management of Gubb & Inggs decided to rationalise their present system of scouring and carbonising. This involved integration of the firm's biological degradation ponds into the *scouring* loop, and on Washline 4, water from the ponds was also used in the first bowl in the separate *desuinting* loop. The advantage of using water from the ponds to cleanse the wool in the first three bowls is that theoretically as much water can be used as required, and carry-over of the contaminants to the rinse bowls minimised without in any way affecting fresh water consumption. (From a grease recovery and detergent point of view, however, too much dilution is a disadvantage, and a compromise has therefore to be found.)

5.2 DYNAMIC ULTRAFILTRATION OF LIQUOR FROM THE RINSE BOWLS

A schematic diagram of the wool rinse effluent treatment process is shown in Figure 5.1.

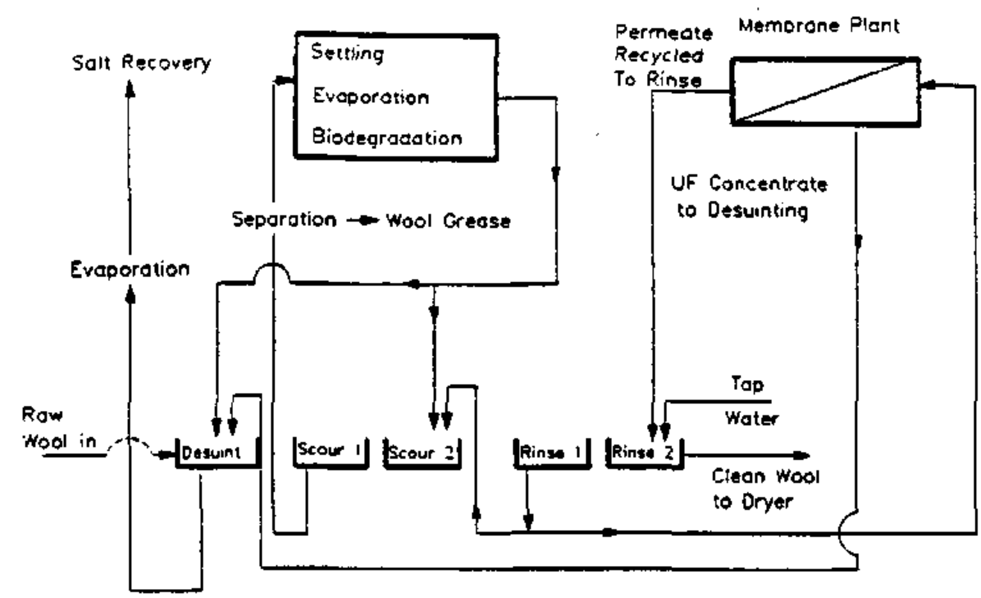

FIGURE 5.1 : Simplified Diagram of Wool Rinse Effluent Treatment Process

The raw wool enters at Bowl 1 and the clean product exits at Bowl 5. Clean water enters at Bowl 5 and flows in the opposite direction. The first bowl (desuinting bowl) uses cold water recycled from the settling ponds together with the concentrate from the membrane plant. As its name implies it removes a large proportion of suint from the wool and also a large amount of the sand and dirt. The next two bowls (scouring bowls) utilise the flow-back from the rinse bowls blended with de-greased water recycled from the settling ponds. These two bowls operate at 60 °C and remove the bulk of the grease and the bulk of the remaining impurities. The last two bowls (rinse bowls) function to remove the remaining grease, suint and dirt contaminants. The dirty water from Bowl 4 is pumped to the membrane plant and the permeate is recycled to Bowl 5, where it is blended with the municipal supply.

5.2.1 Industrial Trials on Washline 4

Using the configuration illustrated in Figure 5.1, approximately 300 000 kg of raw wool, varying in quality from *Snow Whites* to *Stained Lox*, were successfully processed on the Gubb & Inggs Washline 4 over a continuous period of approximately six weeks. A total of 5,4 litres of municipal water, 9,6 litres of water from the biological degradation ponds and 3,1 litres of permeate per kg of raw wool was used during this period. The desuinting operation was carried out using 1,9 ℓ/kg raw wool. The consumption of fresh water on Washline 4 was *halved* from its traditional usage of about 10 ℓ/kg raw wool. Furthermore the quality of the wool product passed all the firm's requirements.

During the above trial approximately 1 million litres of permeate was produced at an average flux rate of 52 ℓ/m^2h. Individual flux rates for the membranes varied widely, but were also shown to decline rapidly with time.

5.2.2 Bacterial Growth

It was noticed that bacterial slimes were forming on the modules and on the walls of the module trays. Checks on the bacterial count of the rinse liquor feed also revealed relatively high counts of bacterial colonies. The bacterial organisms were identified as those belonging to the Sphaerotilus group (*Sphaerotilus natans*).

In some trials the feed liquor was dosed with calcium hypochlorite, but this only suppressed bacterial activity to approximately 300 colonies per $m\ell$. Subsequently the feed liquor was dosed (100 mg/ℓ) with a biocide (Anikem 7330) which proved effective in suppressing bacterial growth to below 10 bacterial colonies per $m\ell$.

However, despite control of bacterial growth, the effects of bacterial control on flux were inconclusive, and flux decline was still marked.

5.2.3 Flux Rates

Flux rates are illustrated in Figure 5.2 which shows the rate of flux decline with time when the feed was dosed with 100 mg/ℓ of Anikem 7330. Starting fluxes were generally between 100 and 150 ℓ/m^2h, but deteriorated over a period of about three weeks to between 20 and 30 ℓ/m^2h. It also proved difficult to maintain a steady-state situation on the plant as a whole since this required stripping and reforming the membranes around every 10 working days. This required frequent utilisation of skilled personnel in the factory who, in the production environment, were not always available. It was considered that if such a stripping and membrane reforming could be *automated* on a similar cycle, the plant flux would average at least 80 ℓ/m^2h.

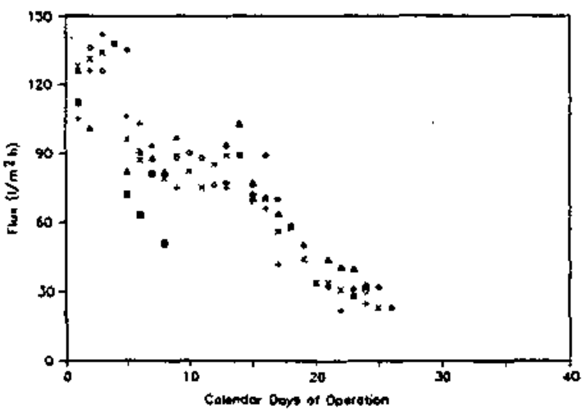

FIGURE 5.2 : Deterioration of Flux with Time

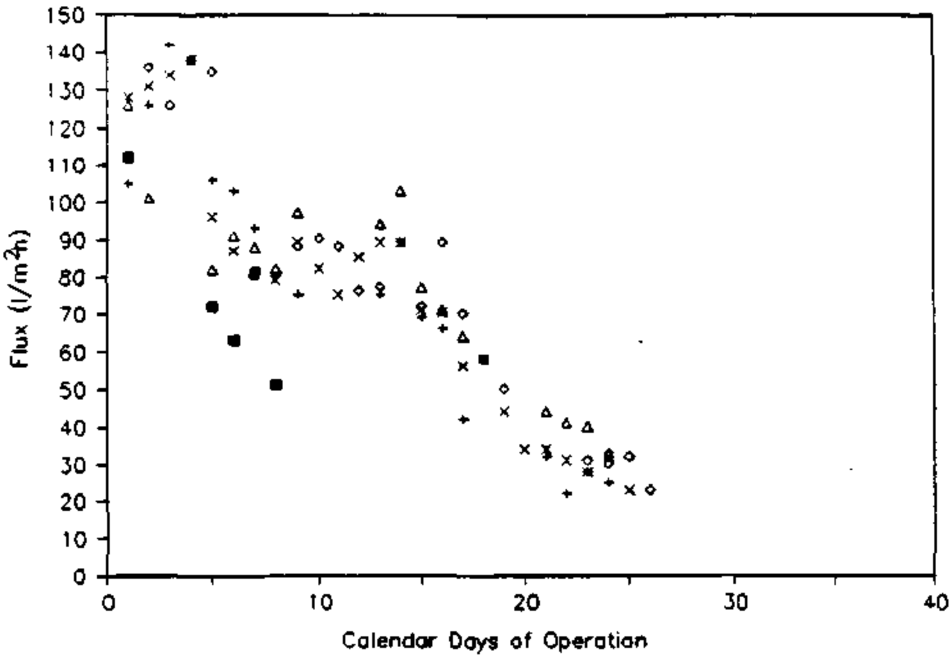

FIGURE 5.2 : Deterioration of Flux with Time

CHAPTER 6
AUTOMATION OF THE MEMBRANE FORMATION PLANT AND RESULTS OF INDUSTRIAL TRIALS

6.1 AUTOMATION OF THE MEMBRANE FORMATION PLANT

In view of the problems outlined above it was decided by the project Steering Committee to design and build, with the assistance of the Pollution Research Group of the University of Natal, and Steffen, Robertson and Kirsten, Consulting Engineers, an automated facility for membrane stripping, substrate cleaning and membrane re-forming.

A schematic diagram of the automated membrane forming plant is shown in Figure 6.1.

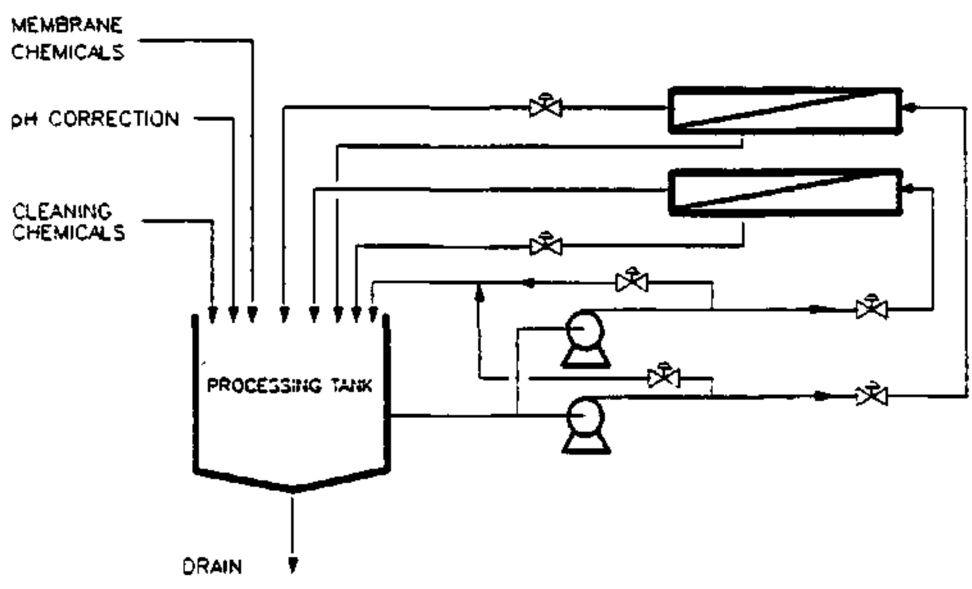

FIGURE 6.1 : Simplified Schematic Diagram of Membrane Plant Showing only Main Process Lines

The membrane reformation procedure consists primarily of the following operations :

(i) removal of the accumulated fouling material by chemical and physico-chemical means.

(ii) removal of the fouled membrane.

(iii) further *polishing* of the sintered porous stainless steel surface.

(iv) circulation and deposition, under stringent pH control, of the membraning suspension through the clean porous stainless steel module.

In order to accomplish the above, the membrane reformation plant is designed to provide for two complete cleaning cycles which consist of a sodium hydroxide wash (with addition of hydrogen peroxide), followed by a nitric acid wash. The cleaning chemicals are rinsed from the system between each chemical addition. The concentration of the cleaning agents is approximately one molar and cleaning solutions are prepared automatically by addition of preset quantities of concentrated acids and alkalis. The cleaning is carried out at 80 °C, the temperature being maintained by a steam heating coil.

After the tube bundles are cleaned, membrane formation is accomplished in two stages by circulation of suspension of hydrous zirconium (iv) oxide under two different conditions of pH. Initially, the circulation is carried out at a pH of approximately 6, at which pH the particle size of the suspensions is comparatively large, and the suspensoid is able to plug the larger pores of the stainless steel substrate (Neytzell-de Wilde and Townsend, 1989). After the completion of this precoating stage the suspension is discarded and a new suspension is circulated at pH 3,6 to 4,0 at which pH the particle size of the suspensoid is such that it can only be detected by light scattering methods. This suspension forms the hydrous zirconium (iv) oxide membrane, which has ultrafiltration properties.

The entire operation is controlled by a programmable logic controller consisting of 28 digital inputs, 4 analog inputs and 32 digital outputs. The programme for the controller incorporates decision-making capabilities which control the duration of the membrane formation process.

The implementation of automated membrane formation has, to a large extent, removed the need for frequent attention of skilled personnel during the stripping and reforming process.

6.2 RESULTS OF INDUSTRIAL TRIALS ON AUTOMATED MEMBRANE PLANT

6.2.1 Flux Rates

Point fluxes for all individual modules of the plant are shown for July and August 1991 in Table 6.1a and September to October 1991 in Table 6.1b. Table 6.1c gives the average values pertaining to the aforementioned four months of operation. Times of stripping and reforming of the individual modules are indicated by asterisks. Unfortunately during this period the frequency of stripping and reforming was only once every 16 working days, instead of the targeted 10 days, with the result that fluxes were below par. In addition, occasional breakdown of one of the high pressure pumps (e.g. on October 4th) caused serious fouling and semi-permanent flux decline.

TABLE 6.1a

Point Fluxes for 10 Modules - 04 July to 29 August 1991

Month	Day	308	428	426	429	425	307	427	424	306	304	Temp
July	04	35	28	21	20	24	23			*58	27	
	05	51	45	43	31	43	34		*176	64	32	
	08	58	50	53		49	36		124	53	31	
	09	75	61	64		56	40		111	50	32	
	10	71	54	57	*83	54	44		112	47		
	11	72	50	58	57	51			97	43	*118	
	12	66	46	72	49	48	*105		92		88	
	15	57		48	44	53	58		74	*70	83	
	16	57		51	52	44	66		87	88	72	
	17	80		73	69		88		135	114	103	
	18	71	*62	63	57		72		01	96	80	75
	19	60	48		46	*91	59		91	83	69	59
	22		49	*154	46	69	62		94	80	67	72
	23		45	101	45	66	55		89	85	64	70
	24		42	90	46	60	48		78	72	59	62
Aug	25		43	89	42	59	48		74	69	56	61
	05		30	65	34	47	38		56	42	41	44
	06	*54	34	65	30	39	35		61	40	40	45
	07	55	41	76	36	44	40		62	49	47	50
	08	41	35	63	29	38	31		64	41	39	43
	09	45	31	61	26	38	31		61	36	38	41
	12	29	33	56		32	27	*55	55	35	36	40
	13	43	36	64		37	30	42	59	38	45	44
	14	42	35	59		36	30	38	58	36	37	42
	15	47	37	65	*113	40	31	42	62	43	40	52
	16	41	38	64	88	39	*99	50	60	40		56
	19	46		63	85	40	89	46	67	38	*96	63
	20	56		87	102		74	52	81	60	74	73
	21	63	*89	97	104		95	57	91	70	78	83
	22	64	76	97	97	*67	87		86	73	78	81
	23	59	73	88	94	52	79		81	61	69	62
	26	42	57	64	70	38	68		59	46	51	51
	27	52	62	80	90	45	72		87	55	62	60
	28	57	74	90	92		78	*86	82	62	67	65
	29		53	67	68	*58	56	57	61	50	50	66

* Denotes new membrane.

TABLE 6.1b
Point Fluxes for 10 Modules - 02 September to 25 October 1991

Month	Day	308	428	426	429	425	307	427	424	305	304	Temp
Sept	02	48	54	71	63	57	56	60	68	*95		56
	03	61		85	87	70	67	70	81	94	*98	62
	04	57		83	85	65	66	67	70	88	80	60
	06	52		83	84	62	65	64	75	83	76	60
	06	45	*96	68	73	50	46	57	66	70	62	68
	09		59	54	55	37	37	42	51	53	47	54
	10		77	73	77	51	52	57	71	70	65	61
	11	*64	72	75	75	50		58	70	67	60	61
	12	61	66	77	80		*96	60	72	68	61	57
	13	53	60	72	72	*64	73	53	63	56	52	56
	17	42	51	60	57	46	57	48	55	45	41	72
	18	35	37	54	46	35	47	37	45	41	36	70
	19	36	43	58	57	37	43	37	54	36	35	56
	20	35	52	64	62	37	46	38	60	37	35	61
	23	25	37	44	37	22	28	18		20	20	57
	24	27	46		61	32	36	31	*111	29	27	65
	25	23	40		59	29	34	29	99	26	27	65
	26	25	60	*94	58	35	42	29	106	32	34	65
	27	17	31	89		24	24		95	18	18	75
	30	14	27	93	*111	21	22		120			70
Oct	01	12	22	75	84	20	18		92			63
	02	9	21	66	91	18	18		88	**143		69
	03		13	40	72		14	19	59	133	20	66
	04	**134	13	46	82		13	34	85	124	18	71
	07	89		30	61	**90	8	15	38	92	13	63
	08	90	*73	26	60	91		14	32	86	10	60
	09	78	51	16	46	96	*62		22	71		61
	14	19	17		15	22	16		7	18	*108	70
	15	30	25	*116	34	39	18			29	53	69
	17	34	33	89	*94	60	24		*72		60	68
	18	32	31	76	91	49	25		59		60	60
	21	26	29	68	85	40	28		57	*116	57	69
	22	30	29	70	77	40	33		54	89	58	68
	23		31	72	85	47	37	*97	58	102	61	66
	24	*139		74	95	50	33	100	70	101	75	71
	25	102	*70	68	84	44		90	61	97	65	65

* Denotes new membrane.

** Denotes new membrane after H_2SO_4 clean.

TABLE 6.1c
Average Flux Data over the Period July to October 1991

	308	428	426	429	425	307	427	424	305	304	Temp
Average flux	51	46	49	66	47	48	50	75	64	54	Av. 62
Std. dev.	25	18	21	24	17	23	21	26	28	24	S.D. 10
No. of days operational	61	61	67	65	63	67	35	68	66	64	
No. of times re-membraned	4	5	3	3	5	4	3	3	5	4	
Grand av. flux	47										
Std. dev.	10										

From the results in Tables 6.1a, b and c it can be seen that there was a relatively high between-module flux variability in spite of the fact that membrane stripping and reforming had been carried out with a high degree of reproducibility. Furthermore, some modules e.g. No. 424, maintained high flux rates for some considerable time, while other modules started with much lower fluxes after stripping and cleaning, e.g. No. 428, and slowly deteriorated with time. It is thought that this could partly be due to inherent variations in the pore size and available pore area of the substrate of individual modules, as well as individual sections of each module, but it was suspected that, in spite of the severity of the cleaning process, some of the foulant remained as an integral part of the substrate.

6.2.2 Flux Fluctuation During Batch Treatment

A typical concentration cycle during which 85 % of the water was recovered, lasted about 1,75 h and produced approximately a four-fold increase in the level of *grease* and *suint* contaminants and a seven-fold increase in *dirt*. Nevertheless, no deterioration of the flux rate could be detected during any specific concentration cycle no matter what the age or condition of the specific membrane, as can be seen from the results obtained in Table 6.2. These results are in contrast to that obtained for scour effluent previously.

TABLE 6.2
Flux Rate Fluctuation During a Batch Treatment Cycle

Time elapsed (from start of new cycle (mins)	Flux rate (ℓ/m^2h) (Measured on Different Membranes at Different Ages)											
	423	304	427	307	304	424	429	426	306	308	304	425
15	55	46	55	63	74	75	71	73	58	42	37	41
30	54	46	56	66	75	74	71	73	57	40	37	41
45	55	48	56	66	76	94	71	74	57	40	37	40
60	56	48	57	65	76	80	71	74	58	40	37	40
75	56	50	56	63	76	77	71	78	58	40	39	38
90	56	49	58	63	75	84	73	74	59	37	37	38
105	57	50	56	65	76	62	71	70	59	38	35	38
120	57	49	56							38	35	38
135										36	37	39
Average (days)	9	13	2	19	2	59	53	29	11	5	11	3

6.2.3 Foulant Removal

In following up the concept of a *difficult-to-remove* foulant, some of the modules were stripped in the normal way and then totally immersed in concentrated sulphuric acid for up to three hours, rinsed and returned to the automated membrane plant for membrane reforming. The dirty sulphuric acid was then transferred to the Company's acid-cracking facility where it was utilised for acid cracking in the normal way.

Table 6.1b shows the results of sulphuric acid treatment on modules 308, 425 and 305 during October. The resultant flux improvement was dramatic, especially on module 308 and 305, with little or no obvious deterioration in permeate quality. Whether this foulant was related to earlier trials on scour effluent and would not re-occur was not possible to say at this stage.

It was interesting to note that after the sulphuric acid-treated modules 308 and 305 had fouled, normal stripping and remembraning restored the flux to the new high levels in the case of module 308, and to a very good level in the case of module 305.

On the strength of the above observation it was decided to implement a programme of regular, occasional, cleaning with concentrated sulphuric acid.

6.2.4 Quality of the Rinse Liquor Feed and Permeate

Tests carried out on the quality of the feed liquor and the quality of the resultant permeate were taken over a period of several weeks, and these results are given in Table 6.3, together with the calculated reduction percent.

TABLE 6.3
Quality of the Feed Liquor and Permeate

Parameter		Feed	Std. Dev.	Permeate	Std. Dev.	Reduction (%)	Std. Dev.
Grease	(mg/ℓ)	514	249	147	47	66	15
Suint	(mg/ℓ)	1 399	459	437	128	67	7
Dirt	(mg/ℓ)	453	264	0	0	100	0
Total solids	(mg/ℓ)	2 366	916	584	136	73	8
Conductivity	(μmhos/cm)	1 102	239	604	97	44	8
COD	(mg/ℓ)	2 404	987	234	37	89	3
Turbidity	(Formazine U)	679	305	5	8	99	1
Detergent	(mg/ℓ)	130		110		6	
Absorbance at	350 nm	1,701	0,454	0,134	0,036	92	
	400 nm	1,148	0,411	0,071	0,027	94	
	450 nm	0,757	0,359	0,042	0,027	94	
	500 nm	0,550	0,324	0,029	0,018	95	
	550 nm	0,431	0,297	0,022	0,016	95	
	600 nm	0,351	0,272	0,016	0,013	95	
	650 nm	0,294	0,252	0,012	0,011	96	
	700 nm	0,243	0,234	0,009	0,009	69	
Temperature	(°C)	69		65			
Pressure	(MPa)	4,2	0,1	2,8	0,2		
pH		8,4	0,4	8,3	0,2		

Values for *Grease*, *Suint* and *Dirt* were obtained by extraction of the liquor and permeate samples with carbon tetrachloride and ethanol. In these tests any dirt accumulated at the interface, and water-soluble matter or *suint* in the water/ethanol layer. The carbon tetrachloride layer may, however, have also contained some detergent. Detergent in the permeate was measured using a modified cobaltothiocyanate technique (Turpie and Van der Walt, 1977).

The feed was characterised by relatively high absorbance values at the lower end of the visible spectrum and with lower values as the wavelength increased. The total solids were largely made up of water-soluble matter, with smaller amounts of *grease* and *dirt*. Conductivity averaged about 1 100 μmhos/cm and turbidity about 680 Formazine units. COD averaged about 2 400 mg/ℓ.

The membranes rejected all the dirt, and about two thirds of the *grease* and *suint*. The conductivity was reduced by 44 %, the turbidity by 99 %, the COD by 89 % and the absorbance from 92 % at the lower wavelengths to 96 % at the higher levels. It should be noted that for rinsing purposes the colour of the water is of prime importance, and therefore the high colour rejection was of special significance. About 94 % of the detergent present in the feed could be detected in the permeate. This in turn was also of significance since a low concentration of detergent in the rinse water could actually be beneficial. There appeared to be no significant change in pH. The temperature of the feed averaged 69 °C, and that of the permeate 65 °C. Inlet pressure averaged 4,2 MPa and outlet pressure 2,8 MPa.

Values for standard deviation indicated that both feed quality and permeate varied quite widely in their characteristics. Nevertheless management indicated that the overall product quality was acceptable for re-use in blends with municipal water for the purpose of rinsing of the scoured wool product.

6.2.5 Water Consumption

Experience with the use of water from the biological ponds since the previously referred to industrial trial has shown that it contains sufficient residual detergency and alkalinity such that adequate scouring can be achieved even if the amount previously used is reduced by as much as one half. This is important from the point of view of reducing centrifugal throughput requirements as well as grease yield. Another advantage has been that total usage of soda-ash by the Company has been reduced by approximately 40 %.

Latest results on water consumption, monitored for some 50 operational days, are given in Figure 6.2. These show that while a total of approximately 11,5 ℓ/kg was required to wash the various qualities of raw wool passing through Washline No. 4, usage of Towns water was only 5,3 ℓ/kg. This represents a saving of approximately 50 % on the Town's water usage traditionally associated with this washline. The amount of water from the biological ponds averaged 4,7 ℓ/kg compared with 9,6 ℓ/kg reported previously. The amount of permeate used amounted to 1,6 ℓ/kg, thus indicating that a total of 6,9 ℓ of *clean* water was used for rinsing per kg of raw wool. Again the quality of the wool product passed all the firms requirements.

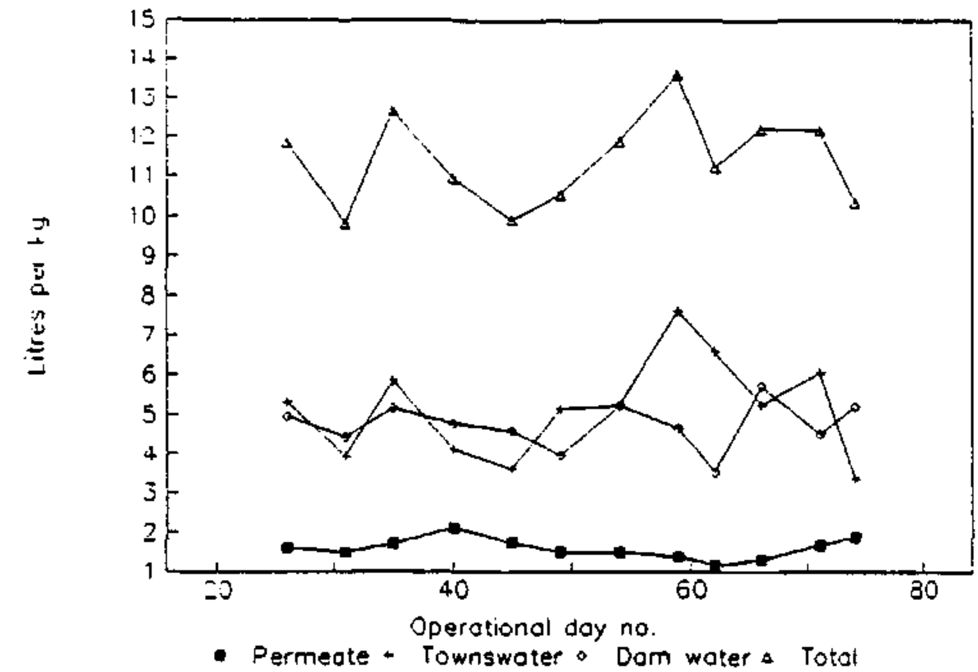

FIGURE 6.2 : Simplified Schematic Diagram of Membrane Plant Showing only Main Process Lines

6.2.6 Recent Recurrence of Low Fluxes

As the drought in the Eastern Cape becomes increasingly serious, the Company has deliberately increased the usage of water from the biodegradation ponds. At the same time membrane fouling has become serious, and even though high flux rates can be obtained by pre-treatment of the modules with concentrated sulphuric acid, flux rates plunge to low levels in a very short space of time. Average weekly fluxes are now about half the targeted amount. The reason for this can only be the deterioration in the quality of the rinse liquor being fed to the membrane plant, and is regarded in a very serious light from the point of view that production of permeate has fallen sharply.

6.2.7 Ceramic Modules - A Possible Alternative

Following initial investigations by the Pollution Research Group of the University of Natal, a ceramic module (IP19-40) having a pore size of 0,1 μm was membraned with a standard hydrous zirconium (iv) oxide membrane, and connected into the ultrafiltration loop of the Modular Demonstration Plant (Townsend, 1991). The module was connected to the return line to the batch processing tank, downstream of the back-pressure control for the high pressure system. The pipe-work and valve configuration was such that the inlet and outlet pressure at the module could be controlled at 500 kPa and 300 kPa, respectively. In spite of various shortcomings with regard to cleaning, which had to be manually controlled every day in order for the chemical clean to be effective, the flux rate per unit area of membrane surface was generally considerably higher than that of the porous stainless steel ultrafiltration modules. At the same time the quality of the permeate was fair. A few spot checks on absorbance indicated that values for the permeate were considerably higher than those for the stainless steel modules at the lower wavelengths. For example, absorbance rejection as about 81 % at a wavelength of 350 nm compared with 92 % for the stainless steel. Rejections above a wavelength of 550 nm were, however, comparable. There was little or no rejection of conductivity, but at all times the permeate was completely clear of all suspended and emulsified matter.

While it is acknowledged that the above experiment should be scaled up and studied for a longer period before drawing any conclusions, it can be said that the ceramic module has the potential to perform relatively well on effluent from the rinse water obtained in a wool scouring operation, whilst being able to operate at only 10 % of the pressure required for the stainless steel modules. Remembraning such a module with perhaps a thicker zirconium oxide membrane could perhaps produce the permeate quality desired, while still producing a very attractive flux at low pressure.

CHAPTER 7
ECONOMIC CONSIDERATIONS

Figures recorded by the Company and which relate to all costs incurred or estimated over the past year, together with permeate production over the same time period, are presented in Table 7.1.

TABLE 7.1
Running Costs of Dynamic Ultrafiltration Plant

	Rand/kℓ Permeate
Cleaning chemicals	2,06
Maintenance	4,46
Major repairs	1,88
Labour	2,47
Electricity	2,66
Steam	2,54
TOTAL	16,03

The total volume of permeate produced was 11 443 kℓ i.e. an average of 46 kℓ/day.

During the next year breakdowns were much less frequent and it appeared as if the major engineering problems had now been overcome. This resulted in a significant reduction in the costs of maintainence, repairs and labour. Revised estimates of the cost of electricity and steam were also carried out. Against these revised costs were offset estimates relating to savings in municipal water costs, potential recovery of an estimated 50 % of the steam energy, and the savings on pumping and handling costs of an equivalent volume which would normally have been returned to the evaporation ponds. The revised estimate was made up as follows :

TABLE 7.2 **Revised running Costs of Dynamic Ultrafiltration Plant**	
	Rand/ℓ Permeate
Cleaning chemicals	2,06
Maintainence	1,96
Major repairs	1,28
Labour	1,57
Electricity	1,80
Steam	3,54
Subtotal	12,21
LESS	
Cost of municipal water	1,34
Potential recovery of energy	1,77
Saving in effluent handling	0,50
Subtotal	3,61
TOTAL	8,60

From the above running costs can be subtracted the cost of one kℓ of municipal water which it replaces, namely R1,34

CHAPTER 8
SUMMARY AND CONCLUSIONS

In an attempt to reduce fresh water consumption in an area suffering from water shortages, while at the same time not sacrificing any deterioration in the quality of its products, an Agreement was entered into between the Company, the Water Research Commission and the University of Natal to embark on a project involving the treatment and recycling of dirty water from its wool scouring operation by means of dynamic ultrafiltration in a batch-operated process. Purification was undertaken by means of formed-in-place hydrous zirconium (iv) oxide membranes which were deposited on stainless steel supports.

The high level and nature of the contaminants removed from raw wool in the early stages of scouring made treatment of the early stage water difficult, and the permeate was of poor quality. While dynamic ultrafiltration of this liquor was *technically feasible* the reclaimed water could *not* be used in the production environment for rinsing.

A switch to the treatment of dirty rinse water proved successful from the point of view that most of the colour, all the dirt and two thirds of the remaining contaminants could be removed. However, stripping and reforming of the membranes was required rather frequently to maintain an acceptable flux. Automation of the stripping and reforming operation followed, as well as the introduction of recycle of water from the Company's biological degradation ponds for use in the early stages of scouring and neutralising. This has now enabled the Company to *reduce its consumption of fresh water by approximately half* on selected washlines, *and its consumption of soda-ash* for scouring and neutralising *by 40 %*, while at the same time *maintaining is product quality*.

At the end of each batch treatment the membranes were automatically cleaned with hydrogen peroxide and rinsed before the next cycle, but fluxes gradually deteriorated with time. It became clear that certain foulants became embedded in the substrate and were impossible to remove. Stripping and reforming of the membranes restored the flux to levels which were far below expectations, some modules performing far worse than others. It was shown that an occasional total immersion in concentrated sulphuric acid could remove this foulant and produce a dramatic improvement in flux without a deterioration in permeate quality. Of considerable concern however is the rapid decline which can be experienced even after sulphuric acid treatment in the present situation where the severe drought has forced the Company to increase the usage of recycled water from the biodegradation ponds. Some foulants, as yet unidentified, would appear to be the cause of the unusually low fluxes being experienced at the present time.

Estimates of running costs taken over a period of one year have shown that it costs some R16 to treat one kilolitre of water and recycle it to the plant. Daily production of the demonstration plant has averaged 46 kℓ. Potential production, if one could eliminate the present foulant, could possible be increased by 80 kℓ/d. Even so the cost of treatment appears prohibitive.

Limited trials with a ceramic substrate and zirconium oxide membrane indicate that high fluxes of reasonably good quality permeate may be possible at operating pressures of only 10 % of that presently used in the plant, but more work is required in this area.

Certainly, from the breakdown of costs given on the use of the stainless steel system used in this investigation, serious breakdowns are too frequent, maintenance costs are far too high, as also is the consumption of electricity and steam. Use of a low pressure system would undoubtedly have certain advantages and would seem worth pursuing. Redesign of the module arrangement and module trays to increase efficiency, conserve heat and enable automatic cleaning *in situ* would be an advantage. An increase in the capacity of the batch processing tanks would take advantage of the relatively small change in flux within a batch.

In conclusion, the present plant would not appear to be industrially viable in its present form.

CHAPTER 9
RECOMMENDATIONS

With reference to the **economic** considerations emanating from the use of dynamic membranes on sintered stainless steel supports in a high-pressure system (Chapter 7), these have clearly been most disappointing. At the same time, however, the project has demonstrated the **technical feasibility** of dynamic ultrafiltration as a means of satisfactorily purifying the dirty rinse water from wool scouring (Chapter 6). As mentioned in the concluding remarks (Chapter 8) a low-pressure ceramic membrane system may well be advantageous.

It is, therefore, recommended that further work be carried out on the use of dynamic membranes for the treatment of wool scouring effluent, more specifically on dirty rinse water which, by virtue of its superior quality when compared with that of waste water from the scouring bowls, can produce a permeate which can be readily re-used. Such research should be directed towards improving the economics of the system, and should preferably be concentrated on a low pressure technology. In this respect it is important that a thorough investigation be made into the potential of using ceramic membranes. Messrs. Gubb & Inggs fully intend to explore this path in the near future under a new project financed by themselves.

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