
**REMOVAL OF COLOUR FROM CAPE WATERS
USING
OZONATION AND MEMBRANE FILTRATION**

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THE REMOVAL OF COLOUR FROM THE SOUTHERN CAPE WATERS USING OZONATION AND MEMBRANE FILTRATION

EXECUTIVE SUMMARY

Many of the natural waters of the southern and western Cape are brownish in colour as a result of the presence of humic and fulvic substances. The use of alum as a coagulant for colour removal is the most common method of treating this water in South Africa. However, this process does have certain disadvantages; relatively high chemical dosages and sludge disposal being two of them.

Two alternative treatment methods, namely ozonation followed by biologically enhanced filtration and membrane separation using nanofiltration (NF) membranes were investigated. Colour removal efficiencies with ozone followed by biologically enhanced sand filtration were better than with ozone followed by biologically enhanced GAC, with up to 95 percent colour removal being achieved. However, the product quality varied and was only below the recommended limit of 20 Hazen in the last 700 hours of operation, when the average colour was 14 Hazen.

NF membranes demonstrated excellent colour removal (to less than 5 Hazen). However, problems were experienced with membrane fouling which necessitated frequent detergent washes of the membranes. The relatively high natural turbidity of the water was identified as the cause of the fouling. Attempts to remove the turbidity in a simple pretreatment step were unsuccessful on the pilot plant.

Compared with conventional treatment methods for colour removal (such as alum coagulation), both the ozonation/biological filtration process and membrane separation were able to reduce the trihalomethane formation potential of the product water to lower values.

An NPV* cost analysis at different nett discount rates over a 20 year plant life showed that the options of ozonation followed by biologically enhanced filtration in GAC and sand filters, would be between 5 and 14 percent cheaper than the conventional alum coagulation method. The product reference unit cost for the two ozone and biologically enhanced filtration systems varied between 60 and 85 c/m³, depending upon the nett discount rate. On the other hand, ozonation only and membrane nanofiltration could be about 55 percent more costly than the alum method, with product reference unit costs of between 108 and 142 c/m³.

It is proposed that the treatment method of ozonation followed by biologically enhanced filtration be investigated further, by conducting a more intensive pilot plant operation aimed at optimizing the biological filtration process for colour removal.

*NPV = Nett present value

It is also proposed that progress with determining the cause and possible prevention of membrane fouling due to humic and fulvic substances be reviewed on an ongoing basis so that any breakthroughs in this area can be applied to the membrane separation option for colour removal.

CONTENTS

	Page No
1. INTRODUCTION	1
2. LITERATURE SUMMARY	3
2.1 Ozonation	3
2.2 Membrane Separation	5
3. EXPERIMENTAL PROCEDURES AND RESULTS	6
3.1 Ozonation Investigation	6
3.1.1 Objectives	6
3.1.2 Experimental procedures with ozone	6
3.1.3 Results of ozonation investigations	13
3.2 Membrane Separation Investigation	26
3.2.1 Objectives	26
3.2.2 Initial membrane selection	26
3.2.3 Semi-technical scale membrane selection - continuous bench tests	28
3.2.4 Pilot study	31
3.2.5 Results of membrane separation investigations	33
3.3 Effectiveness of Conventional Colour Removal Processes	44
3.3.1 Objective and method	44
3.3.2 Findings	44
4. DISCUSSION	46
4.1 Ozonation	46
4.2 Membrane Separation	48

	Page No
5. PRELIMINARY ESTIMATES OF CAPITAL AND OPERATING COSTS FOR FULL SCALE INSTALLATIONS	50
5.1 Ozonation	50
5.1.1 Direct ozonation only	50
5.1.2 Ozonation plus biological treatment in GAC	52
5.1.3 Ozonation plus biological treatment in sand filters	53
5.2 Membrane Separation	55
5.3 Conventional alum dosing followed by sedimentation	56
5.4 Cost summary	58
6. CONCLUSIONS	59
6.1 Ozonation	59
6.2 Membrane Separation	60
7. DISCUSSION AND PROPOSALS FOR FURTHER WORK	62
7.1 Background	62
7.2 Proposal for Further Work	63
8. RECOMMENDATIONS	65
9. ACKNOWLEDGEMENTS	66
10. REFERENCES	67

**ANNEXURE A: REPORT BY HA DE VILLIERS ON SEMI-TECHNICAL
BENCH SCALE MEMBRANE TESTS**

1. INTRODUCTION

Many of the natural river waters of the southern and western Cape and also some of the waters of the eastern Transvaal contain humic and fulvic substances which impart a brownish colour to the water. These organic substances are introduced to the water as a result of extraction from vegetation and plant residuals (Ødegaard *et al*, 1986; World Health Organisation, 1984). Some of these waters also contain unacceptably high concentrations of iron and manganese, which contribute to the colour problems.

The intensity of colour in natural waters of the Cape varies significantly from pale to dark brown. Standard Methods (1981) reports two types of colour, namely, "true colour" and "apparent colour"; the former relating to the colour of the water after all particulate matter has been removed (for example by filtration). The standard procedure for colour measurement is the platinum-cobalt method (Standard Methods, 1981). 1 mg/l Pt-Co is equivalent to 1 Hazen, the unit usually used in South Africa to report colour.

There are several reasons why natural water is treated to remove colour:

- i) Aesthetic. The World Health Organisation (1984) report that most people are able to detect levels of colour above 15 TCU (true colour units) or Hazen units in filtered water. This is in line with the SABS recommended limit of 20 Hazen for potable water (SABS, 1984).
- ii) Taste and odour. The presence of humic substances is often associated with other taste and odour compounds particularly when the water is chlorinated.
- iii) The formation of disinfection by-products such as trihalomethanes (THM's). These substances have been shown to be potential carcinogens (Shukairy and Summers, 1992) and could pose health risks.

The usual methods for colour removal from Cape waters are the well proven techniques of coagulation with aluminium sulphate (alum) or an iron salt, followed by flocculation, sedimentation and filtration. These processes rely on the precipitation of humates or fulvates and/or the adsorption of the colour compounds on the metal hydroxide floc particles. Although the process works well and reduces colour to acceptable levels it relies on relatively

large dosages of coagulant to remove colour and to produce floc with good settling characteristics. Lime dosing is usually required to adjust the pH to the desired range for efficient colour removal and polyelectrolyte flocculants are also often used for aggregation of floc particles and to improve settlement. The area requirements for plants of this type are extensive due to the often poor settling characteristics of the flocs. Furthermore, the process produces fairly large volumes of sludge which generally has poor dewatering characteristics, creating disposal problems.

While existing treatment methods to remove colour using alum are effective, these processes may not reduce the THM formation potential (THMFP) to within acceptable limits. This is illustrated by the findings of Sierka *et al*, (1989) who showed that a water with a low colour level (< 15 Hazen) can still exhibit a significant THMFP. A contributory factor could be the presence of other dissolved organic carbon (DOC) compounds in the water. The degree to which the organic content of natural water is made up of humic/fulvic substances varies according to the literature; 80-90 percent (Grebenyuk, 1989), 50 percent (Sierka *et al*, 1989). At present no statutory limits have been set for THM concentrations in potable water in South Africa, however, the responsible authority is reportedly contemplating the introduction of guidelines (van Steenderen *et al*, 1991).

With the above in mind two alternative processes for the removal of natural colour from water have been investigated, namely ozonation and membrane separation. A desk study had shown that it would be possible to utilise these processes at approximately the same cost as the conventional treatment systems, but without the sludge disposal problem, with a potentially greater reduction in the THMFP and smaller land area requirements; this latter aspect could be of importance when waterworks have to be extended in areas where space is limited.

In order to evaluate the findings of the desk study a project financed by the Water Research Commission has been undertaken to investigate the removal of natural colour from Cape water using ozonation and membrane separation processes. The report presents findings of both laboratory scale investigations and pilot plant studies.

2. LITERATURE SUMMARY

2.1 Ozonation

Ozone is a powerful oxidant and disinfectant, with a thermodynamic oxidation potential that is the highest of all common oxidants (Glaze *et al*, 1987). It is widely used for the treatment of drinking waters and some industrial wastewaters (Yao and Haag, 1991), in more than 1 000 plants worldwide in the early 1980's (Rice *et al*, 1981) and in at least 64 potable water plants in the USA (Rice, 1992).

In simplistic terms, there are two pathways by which ozone reacts with contaminants in water, namely: the direct reaction of ozone (O_3) with the contaminant and the reaction of the hydroxyl radical ($OH^\bullet$) with the contaminant. In pure water ozone decomposes to O_2 through a series of circular chain reactions initiated by hydroxide ions (Glaze *et al*, 1987). Within the chain reaction an $OH^\bullet$ radical is formed and if this reacts with contaminants in the water the chain is broken. Two inorganic species that are efficient radical scavengers are bicarbonate and carbonate. However all contaminants of the water that are capable of reacting with $OH^\bullet$ radicals will compete for the intermediates as the ozone decomposes.

Singer (1990) maintains that the conditions under which the ozone reacts, either by the direct or radical pathway, influences its performance. Consequently the constituents of the water should be carefully considered when assessing the use to which the ozone is put. The direct oxidation pathway is thought to be the method by which ozone reacts best with natural humic substances (Singer, 1990) and therefore the level of natural bicarbonate and carbonate alkalinity would influence the ozone behaviour and by-product formation. It has been hypothesised that molecular ozone is also the most effective disinfection species (Singer, 1990).

It is well known that the addition of a strong oxidant such as ozone to humic waters reduces the colour significantly. Colour reductions of between 70 and 80 percent have been achieved (Ødegaard *et al*, 1986), with the colour being reduced almost linearly with increasing dosages of ozone to a point beyond which the reduction levelled off. Ozone attacks organic molecules at the carbon-carbon double bonds and in that way either cleaves the molecule or alters its structure. For the water studied by Ødegaard it was noted that for optimum colour removal

the ozone dosage relative to the raw water colour was approximately 0,075 mg O₃/mg Pt-Co (equivalent to 0,075 mg O₃/Hazen).

In other more recent work (Tan and Amy, 1991) ozone removed 88 percent of the colour from a natural water at ozone dosages of 1 mg O₃/l per 4-5 Hazen units. They also reported a levelling off of the colour destruction above a given ozone dosage suggesting an ozone-refractory fraction of the colour. In their case with initial colour of about 25 Hazen the refractory fraction was only about 3 Hazen units.

Ozone on its own does not significantly reduce the TOC in natural waters (Adin *et al*, 1991) and this can be important in waters which have a THM imposed limit. Tan and Amy (1991) reported that after ozonation the concentration of THM's was reduced by 76 percent during a 24 hour simulated distribution system test, but the long-term (seven day) THMFP was only 1,5 percent less than that of the raw water. During both tests a positive chlorine potential was maintained for the entire reaction time.

In other work (Myers, 1990) a reduction of 44 percent in THM formation was observed after a three day reaction time with chlorine following pre-ozonation of the raw water. Further conflicting results regarding the effectiveness of ozone to remove THM precursors have been found (Hyde and Zabel, 1986), which indicate that the characteristics of the water and the constituents of the TOC may play an important role.

It is well documented that ozone increases the biodegradability of recalcitrant organic substances. This could be a disadvantage since if ozonation is used as a final disinfection step in potable water treatment then extensive biological re-growth could occur in the distribution system, unless sufficient disinfectant residual is maintained throughout the system. However, if after ozonation the water is filtered through a biologically active bed of porous media (such as sand or granular carbon) then biodegradation of the organics has been shown to occur within the bed (Rice and Robson, 1982). This not only produces a biologically stable water which removes the potential for downstream regrowth but is able to achieve higher organic carbon removals than when using either ozone or the porous media alone (Singer, 1990). Generally the ozone dosages required to improve the biodegradability of the organic substances are in the range of 1-2 mg O₃/mg TOC.

The use of biologically active sand filters in conjunction with ozone to enhance the removal of organic material was first reported in 1904 (Masschelein, 1992). The extension of this method to include biologically active granular activated carbon (GAC) filters was proposed in the early 1980's and numerous reports of ozone-enhanced biological treatment of drinking water now appear in the literature (Singer, 1990).

2.2 Membrane Separation

The removal of naturally occurring organic substances such as humic and fulvic components using membranes has received considerable attention during the past few years (Watson and Hornburg, 1989; Tan and Amy, 1991). A factor that has given impetus to this interest is that many of these substances are precursors for the formation of disinfection byproducts, of which there are a wide variety, and which are potentially harmful substances, as previously mentioned.

Recently attention has been focused on the membrane separation process of nanofiltration (NF) which has advantages over reverse osmosis (RO) for the removal of specific organic compounds, because it is a looser, more open membrane with a lower system operating pressure (Watson and Hornburg, 1989).

Of particular interest regarding the use of membrane separation for colour removal is a comparative study of the organic and inorganic rejection characteristics of eight RO and NF membranes of different types operated on a coloured groundwater in Orange Country, Southern California, USA (Tan and Sudak, 1992). All eight membranes were found to be capable of removing colour from the groundwater and further long-term tests were conducted using two brackish water and two NF softening membranes. Colour removals down to less than 3 Hazen were achieved for feed waters with colour ranging from 65 to 68 Hazen.

Apart from the good colour removal achieved, the membranes were able to reduce the THMFP from about 400 $\mu\text{g/l}$ to about 10 $\mu\text{g/l}$. Of interest too, was the finding that the NF membranes were the most energy efficient and gave as good colour removal results as the "tighter" RO membranes (Tan and Sudak, 1992).

3. EXPERIMENTAL PROCEDURES AND RESULTS

This section is divided into three parts. The first part deals with the ozonation experimental procedure and results, the second deals with the membrane separation experiment and results, and the third deals with the effectiveness of conventional colour removal processes to remove colour and reduce the THMFP of the product water. A discussion of the results obtained during these studies forms section 4 of this report.

3.1 OZONATION INVESTIGATION

3.1.1 *Objectives*

The objectives of the investigations using ozone to remove colour were:

- i) To establish the degree of colour removal that could be achieved with various dosages of ozone.
- ii) To establish the effect of ozone dosage on the UV absorbency at 254 nm.
- iii) To establish the effect of introducing hydrogen peroxide together with ozone on colour removal.
- iv) To establish the effect of ozone and ozone/H₂O₂ on the THMFP of the water.
- v) To establish the effectiveness of ozonation, followed by filtration through a slow sand filter and a granular activated carbon (GAC) filter (operated in parallel), on the degree of colour removal achieved.

3.1.2 *Experimental procedure with ozone*

a) Equipment

A Model 03V10-AR ozonator manufactured by OREC (Ozone Research and Equipment Corporation) was hired for the duration of the study from Aqua Media CC (the local

agents for the equipment). The generator was a corona discharge type and operated on air with a capacity at full load of 4 g O₃/h.

A reactor column was constructed in clear uPVC; it had a diameter of 50 mm and a height of 4 m. A schematic of the plant arrangement is shown in Figure 1. Raw feed water was pumped into the column at the top, and drained from the column at the base. Ozonated air entered at the bottom of the column and flowed counter current to the water. Attached to the top of the column was a gas/liquid separation compartment, from where off-gas samples could be drawn for analysis. Treated water exiting the contact column was collected in a container for sampling and observation.

b) Experimental Technique

i) *Initial Laboratory Study*

The only process problems that were experienced were in controlling the liquid flowrates at fairly low values and coalescence of the ozonated gas in the column under certain conditions.

Once the reactor column had been filled with raw water and the inflow and outflow rates controlled for the particular run, the ozonator air flow was started. The ozonation power was kept off until the air flowrate had been set correctly and the bubble distribution in the column was satisfactory. The ozonator power was then increased to the required percentage setting depending upon the approximate ozone dosage required.

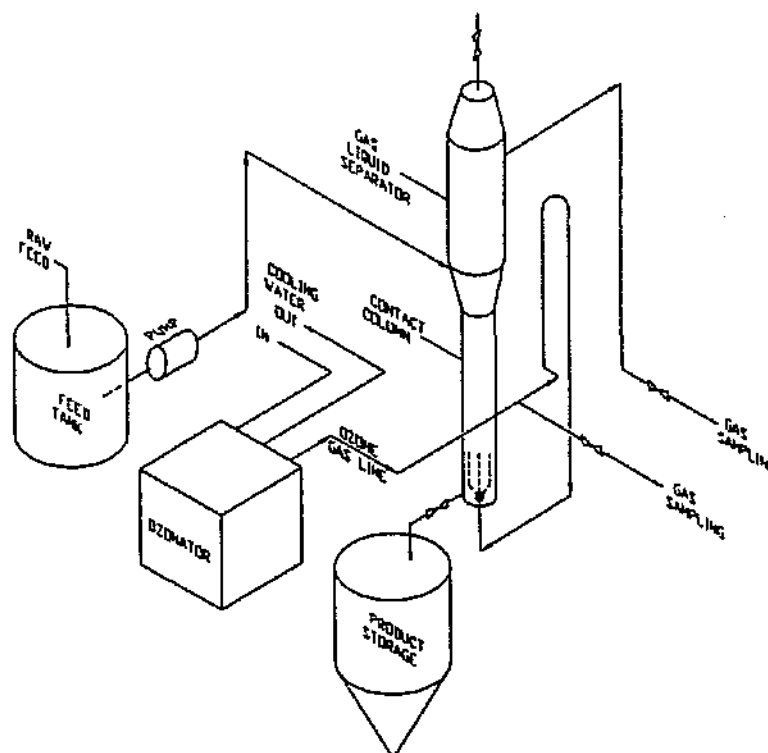
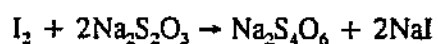
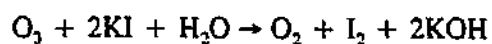


Figure 1 : Schematic arrangement of ozone equipment

After ozone production had started, the reactor was run for approximately twice its hydraulic retention time before the first set of samples were taken. Sample taking also involved recording gas and liquid flowrates and temperatures; gas pressures; ozone concentrations in the inlet and outlet gas and obtaining water samples for chemical analysis.

The determination of the ozone concentration in the gas phase was by the well known iodine/sodium thiosulphate titration technique (Standard Methods, 1981). About 1 g of potassium iodide (KI) was introduced into the gas absorption bottle and dissolved in 200 ml of deionized water. A known volume of air and ozone was then bubbled through the solution, iodine being released as a result of the oxidation of the KI. The resulting iodine solution was then acidified with a few drops of concentrated H_2SO_4 acid and titrated against 0.1 M sodium thiosulphate solution to the end point, using starch as indicator. The relevant chemical reactions are the following:



The equations indicate that one mole of ozone reacts with two moles of sodium thiosulphate. The measurements of the gas flowrates were made at ambient conditions (temperature 12 - 15°C; approximately 1 atmosphere pressure) and the calculation of ozone mass under these conditions was used in the mass balance to determine ozone usage.

Treated water leaving the column was also analysed for ozone residual to calculate the overall ozone usage within the contact column.

To establish the effectiveness of ozone to remove colour from natural Cape water a sample was obtained from the Duivenhoks Water Treatment Works near Heidelberg (Cape). The water had a colour of 200 Hazen and a detailed analysis of the water is presented in Table 1.

TABLE 1: Analysis of water from Duivenhoks Waterworks collected on 12 May 1992

DETERMINANT	UNITS	VALUE
Potassium as K	mg/l	1.3
Sodium as Na	mg/l	25
Calcium as Ca	mg/l	2.2
Magnesium as Mg	mg/l	3.9
Sulphate as SO ₄	mg/l	13
Chloride as Cl	mg/l	40
Alkalinity	mg/l as CaCO ₃	9
Absorbance at 545 nm		0.122
Absorbance at 400 nm		0.473
Absorbance at 275 nm		2.902
Absorbance at 254 nm		3.528
Dissolved Organic Carbon	mg/l	12.5
Total Organic Carbon	mg/l	15
Colour	Hazen	200
Turbidity	NTU	35
Conductivity	mS/m	18.5
pH (Lab)		6.6
Saturation pH (pHs 20°C)		10.3
Total Dissolved Solids (Calc)	mg/l	118
Total Hardness	mg/l	22
CATIONS	meq/l	1.55
ANIONS	meq/l	1.58

A series of batch experiments was carried out at various ozone dosages between 13 and 71 mg/l. The contact times in the column were varied between approximately 10 and 20 minutes and samples of the product and feed water were taken and analysed for colour, absorbance at 254 nm, turbidity and THMFP. The effect of the addition of hydrogen peroxide (H₂O₂) to the feed stream ahead of the ozonation column was also investigated at dosages of between 4 and 26 mg H₂O₂/l.

ii) *Second Laboratory Study*

Prior to starting the pilot plant investigations with ozonation followed by biologically enhanced filtration Prof. Hans Van Leeuwen was commissioned to investigate the biodegradability of a sample of Duivenhoks water following ozonation.

Seven water samples were ozonated at various dosages and the colour intensity measured before and after ozonation. The samples were then inoculated with raw Duivenhoks water and after adding 4 ml of spent GAC stored for a period of 14 days. Total plate counts of the samples were carried out after the storage period in order to give an indication of the biological activity in the samples. This is a measure of the increased biodegradability of the organic matter present in the water as a result of the action of the ozone.

iii) *Pilot Study*

Following the laboratory study the ozonation equipment was moved to Heidelberg (Cape) and installed at the Duivenhoks Works. The operation of the pilot plant different from the laboratory study in that the plant was operated on a continuous basis. In addition, the ozonated water from the contact column was distributed between two filter columns; one containing previously used GAC (approximately 2-3 mm diameter), and the other containing filter sand (effective size of 0,6 mm). The layout of the pilot plant is shown schematically in Figure 2.

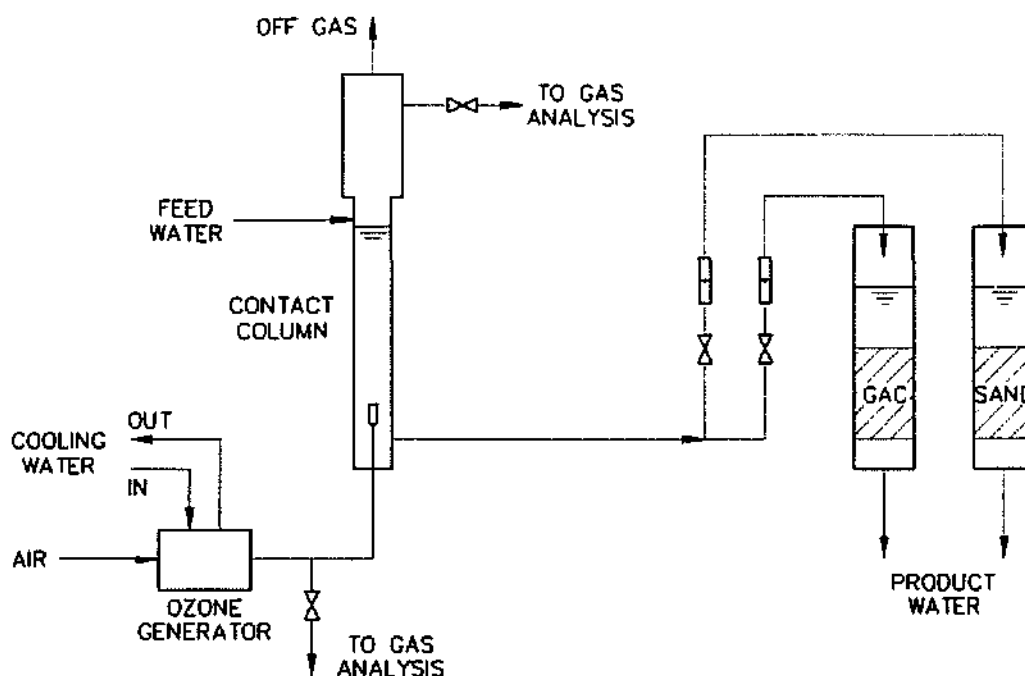


Figure 2: Schematic arrangement of ozone pilot plant

Samples of raw feed water, the ozonated water and the product from each of the filters were collected every six hours and analysed for colour, pH and turbidity by the operating staff at Duivenhoks. The concentration of ozone in the feed gas and off-gas was also analysed every six hours. In addition the flow rates through the contact column and the filters were recorded.

The plant was operated with the filters in the downflow mode at an initial low ozone dosage of 4 mg/l in an attempt to allow biological activity to become established in the two filters. Later in the study the ozone dosage was increased to a maximum reacted concentration of around 25 mg/l. No hydrogen peroxide was added during the pilot study.

Water samples were collected approximately weekly and analysed for DOC, absorbance at 254 nm and alkalinity. Less frequent analyses were carried out for nutrients and two analyses were carried out for THMFP.

3.1.3 *Results of ozonation investigations*

i) Initial Laboratory Study

The tests were carried out over a period of three days. The first day was used to set up and commission the equipment, test the analytical procedures and carry out a few trial runs. The second and third day were used to obtain the experimental data. Table 2 presents the analysis of a composite sample of the raw coloured feed water to the reactor obtained during the test period. A summary of the experimental results is presented in Table 3. The total THM formation potential of 151 $\mu\text{g/l}$ reported in Table 2 was the concentration of THM's produced after a 12 hour contact period with 12 mg/l free chlorine. A reduction in the THM formation potential was assumed to indicate a removal of THM precursors.

Table 3 presents the results achieved with ozonation, using ozone only and with ozone and hydrogen peroxide during runs 9, 10 and 11.

a) *Ozone only*

The effects of ozone only on the removal of colour is shown graphically in Figure 3, which illustrates that the percentage colour removal increased with the mass of ozone reacted, but that this was not a linear relationship. The trend was the same for both filtered (through 0,45 μm filters) and unfiltered product water samples. The lowest colour value that was obtained on the product water was 10 Hazen units, after filtration. Prior to filtration the colour value of this water was 30 Hazen. This corresponds to a colour removal of 85 and 95 percent respectively, from the initial 200 Hazen. The dosage of ozone that reacted to produce this quality of product water varied between 48 mg/l and 71 mg/l. The reacted dosages of ozone agree reasonably well with the dosage ratios observed by Tan and Amy (1991) of 1 mg O_3/l per 4 - 5 Hazen units. According to their observations the required dosage should have been around 42 mg O_3/l .

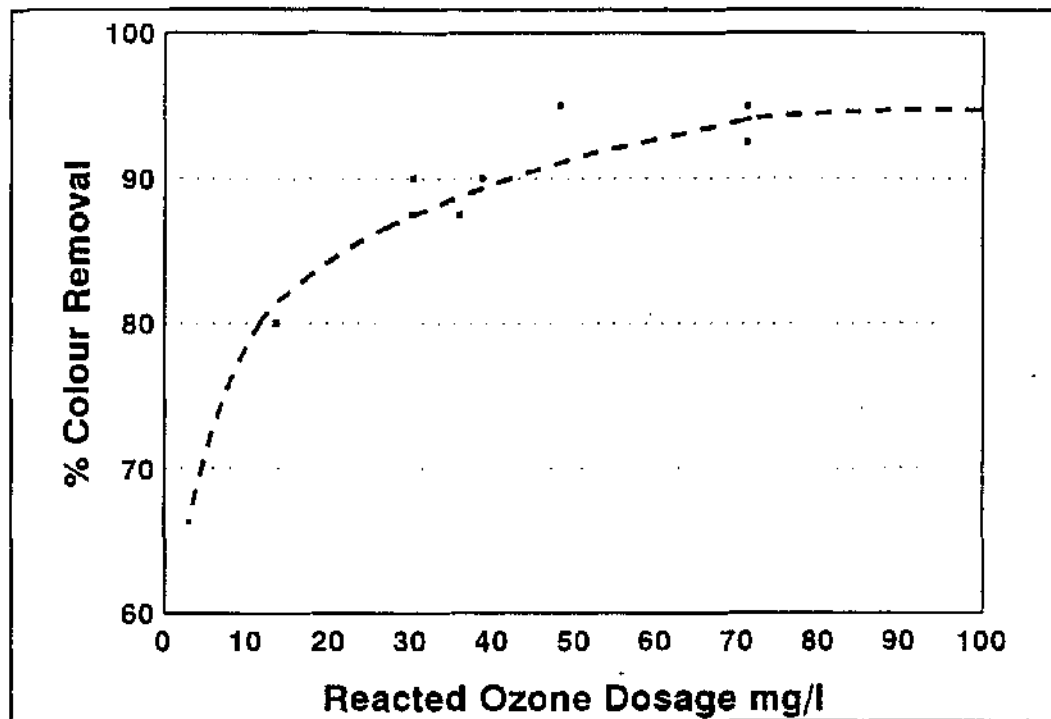


Figure 3: Percent Removal of colour from natural water (initial 200 Hazen) by ozone only

Table 2: Characterisation of raw feed water used during preliminary laboratory ozonation studies, obtained during the laboratory test period

Colour (Hazen)	Turbidity (NTU)	UV Absorbance 254 nm	Total THM formation potential ($\mu\text{g/l}$)
200	5,3	2,927	151

Table 3: Summary of results obtained during preliminary tests to evaluate the use of ozonation for the removal of natural colour from raw water (See Table 2)

Run	Raw Feed Flow rate (l/min)	Hydraulic retention time in contactor (min)	Ozone reacted (mg/l)	Efficiency of Transfer (%)	H_2O_2 dosage (mg/l)	Product Water					Colour Removal		Total THM Precursor Removal (%)	Reduction in UV absorbance 254 nm (%)
						Colour before filtering (Hazen)	Colour after filtering (Hazen)	Absorbance 254 nm	Turbidity (NTU)	THM formation potential ($\mu\text{g/l}$)	Before Filtration (%)	After Filtration (%)		
1	0,81	9,7	13,5	73	0	70	40	1,545	6,9	N.A.	65	80	N.A.	47
2	0,85	9,2	18,3	81	0	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
3	0,82	9,6	35,9	65	0	40	25	1,706	6,9	N.A.	80	88	N.A.	42
4	0,82	9,6	38,6	70	0	40	20	1,067	6,7	N.A.	80	90	N.A.	64
5	0,39	20,4	71,0	57	0	30	10	0,888	6,7	N.A.	85	95	N.A.	70
6	0,41	19,4	48,1	44	0	30	10	0,856	6,7	86	85	95	43	71
7	0,87	9,1	30,3	60	0	40	20	1,086	5,6	30	80	90	80	63
8	0,35	22,5	71,0	57	0	35	15	0,860	6,0	53	82	93	65	71
9*	0,80	9,8	15,3	84	4,2	80	60	1,547	5,6	85	60	70	44	47
10*	0,87	9,1	25,7	81	13,4	30	20	0,912	6,0	38	85	90	75	69
11*	0,89	8,8	39,2	83	25,9	70	50	1,659	7,5	39	65	75	74	43
12	1,02	7,7	30,1	70	0	50	25	1,135	7,0	76	75	88	50	61

* During these runs H_2O_2 was dosed.

N.A.: No Analysis

The product water UV absorbance at 254 nm gives a good indication of some of the changes in the nature of the organic substances in the water that have been brought about by ozonation. Although ozonation is known to have little effect on the total concentration of organics (TOC) the changes in the nature of the organics can be observed by monitoring the UV absorbance at 254 nm and 400 nm (Hyde and Zabel, 1986). Absorbance at 254 nm is a measure of the concentration of the aromatic and aliphatic compounds with conjugated and cumulative double bonds. Ozone destroys the double bonds and reduces the UV absorbance at that wavelength.

As can be seen from Table 2 a composite sample of the raw feed water to the ozone plant had a UV absorption at 254 nm of 2,927. Using this value for the raw water the reduction in absorbance at 254 nm was calculated for the various runs and the values (shown in Table 3) varied between 42 and 71 percent. The highest reductions occurred when the dosage of ozone that reacted was the highest, which corresponded to when product water had the lowest colour content.

In all cases the action of ozonation resulted in an increased turbidity of the water from an average of 5,3 NTU before ozonation to between 5,6 and 7,0 NTU after ozonation. This is thought to be as a result of the formation of microflocs during the ozonation process. Filtration to remove the microflocs improved the colour of the water in all cases as shown in Table 3.

The effect of increasing the hydraulic retention time in the ozone contact column improved ozone uptake and resulted in a better quality product water. However, the transfer efficiency of the ozone to the water at the higher hydraulic retention times was lower than at shorter retention times.

The effect of ozonation only on the removal of THM precursors is not quantitatively conclusive with the limited number of results obtained. However, the reduction varied between 43 and 80 percent. The reduction in THM precursors does not appear to be directly related to the reduction in UV absorbance at 254 nm.

The data obtained for colour removal showed a non-linear relationship between ozone dosage and colour removal; indicating that for this water at relatively low ozone dosages (15 - 20 mg/l) a significant reduction in colour could be achieved.

In this case it appeared that the refractory portion of the colour was equivalent to between 10 and 30 Hazen units, or about 5 to 15 percent of the colour. This confirms what has been found by previous workers (Ødegaard *et al*, 1986 and Tan and Amy, 1991). In this instance the best colour removal relative to the ozone dosage was at a reacted dosage of 48,1 mg/l. This is equivalent to a dosage of 1 mgO₃/4,16 Hazen units which agrees well with the dosage ratios observed by Tan and Amy (1991). In terms of mgO₃/mg TOC a dosage of 48,1 mg/l equates to 3,2 mgO₃/mg TOC.

b) *Ozone and hydrogen peroxide (peroxone)*

Three experimental runs were carried out using different concentrations of ozone together with varying concentrations of hydrogen peroxide, called the PEROXONE process. When compared to runs without the use of peroxide and in which similar quantities of ozone reacted it appears that:

- i) at low dosages of hydrogen peroxide (4,2 mg/l) the removal of colour from the water was slightly less than with no peroxide at all. In this case the ratio of peroxide dosed to ozone reacted was 1 : 3,6.
- ii) at a higher dosage of peroxide (peroxide dosed to ozone reacted ratio of 1:1,9), the reduction in colour was good (85-90 percent), as was the reduction in UV absorbance at 254 nm (69 percent) and the reduction in THM precursors (75 percent). This was almost the same performance as that obtained by a similar ozone dose on its own.
- iii) at the highest dosage of peroxide (peroxide dosed to ozone reacted ratio of 1:1,5) the colour removal and reduction in absorbance were not as good; 65 to 75 and 43 percent respectively. The reduction in THM precursors was, however, still good at 74 percent.

To confirm the effect of hydrogen peroxide and ozone on the colour removal a final run (run 12) was carried out with ozone only. Colour removal and reduction in absorbance improved to 75 to 88 percent and 61 percent, respectively. This indicated that as far as these parameters were concerned ozone alone was better than the combination of ozone and hydrogen peroxide for the case of lowest and highest peroxide dosage. The reduction in THM precursors for run 12 was, however only 50 percent, which was similar to that achieved at the lowest hydrogen peroxide dosage.

What was clearly evident during the addition of the peroxide was the consistently high transfer efficiency achieved for the ozone (81 to 84 percent) when hydrogen peroxide was present. This is what would be expected because of the reaction between the ozone and hydrogen peroxide to produce a higher concentration of hydroxyl radicals. During the tests with hydrogen peroxide the hydraulic retention time was relatively short at between 8,8 and 9,8 minutes. Longer retention times were not investigated.

The pH and alkalinity of the raw feedwater were approximately 6,5 and 10 mg/l as CaCO_3 , respectively. Under these conditions it is expected that with ozone alone the direct reaction pathway would probably dominate because of the relatively low pH. However, the addition of hydrogen peroxide to the water during ozonation would produce many hydroxyl radicals, which because of the low alkalinity would not be consumed quickly and therefore the radical pathway would be expected to dominate. This would help to explain why overall the colour removal by the combination of ozone and hydrogen peroxide was no better than with the same dosage of ozone alone.

ii) Second Laboratory Study

The results of the test work conducted independently by Prof. Hans Van Leeuwen confirmed the results of the initial laboratory scale investigations discussed above, using ozone alone for colour removal.

The investigations into the biodegradability of the Duivenhoks water showed that ozonation of the water resulted in significantly greater 48 hour total plate counts

for samples taken after 14 days of storage than was the case when the water was not ozonated. These results indicated that the organic constituents in the water were more biodegradable after ozonation. Colour removal did take place during the storage period of the samples, and up to 40 percent of the remaining colour was removed.

Although the colour removal was not spectacular during this test work, the results confirmed the favourable effect of ozone on the biodegradability of the water which was the main purpose of the investigations.

iii) Pilot Plant Study

The ozone pilot plant was operated for a period of 3 300 hours (four and a half months). Initially time had to be allowed for biological activity to become established in the filter media and for the first two months of operation the reacted ozone dosage was kept low, at an average of 4,3 mg/l. As expected the removal efficiency after ozone addition averaged only 12 percent during this period and overall colour removal after the GAC and sand filters averaged 22 percent and 24 percent, respectively.

After about two months of operation an improvement in colour removal in the two filters was observed; the removal efficiency increasing to approximately 55 percent. This was taken to indicate the establishment of biological activity within the filters. A significant drop in the concentration of DOC in the product from the filters (from 11 mg/l to approximately 6 mg/l) seemed to confirm these observations. Biological growths on the inside of the clear PVC filter columns were noticeable as well as what appeared to be a layer of biological matter on the top of the sand in the sand filter.

Approximately 100 hours later (after a total operating time of about 1 800 hours) the ozone dosage was increased to give a reacted ozone dosage of between 10 and 15 mg/l. The colour level of the water after ozonation and after the filters continued to drop with about 60 percent being removed in the ozonation step. The colour of the product water from the two filters was variable but similar, dropping to 25 Hazen on occasion, but averaging about 40 Hazen between 1600 and 1900

hours of operation. This amounted to an average of 80 percent reduction for the combination of ozonation and biological filtration treatment. The reacted ozone dosage and colour of the water leaving the two filters is shown in Figure 4.

At approximately 1900 hours (indicated by the arrow in Figure 4) an operator error during backwashing of the filters caused a loss of both GAC and sand. Most of the GAC was recovered and replaced but it is obvious from the figure that this incident affected the quality of the filtered water. The colour of the water from the GAC filter increased to 85 Hazen and that of the sand filter to 75 Hazen. To compensate for the loss of filter media the flow rate of raw water to the contact column was reduced, as was the flowrate of the ozone/air mixture to keep the ozone dosage constant.

Unfortunately these adjustments resulted in further hydraulic changes within the process. The contact time in the ozone reactor doubled from approximately 2,5 minutes to approximately 5 minutes, but this did not appear to influence the colour removal that was achieved by ozonation only, which remained at about 60 percent. As expected the increased contact time in the reactor together with the lower ozone/air gas flowrate improved the transfer efficiency in the column which increased from approximately 80 percent to 91 percent.

The contact time in the filters also changed as a result of the hydraulic changes. The empty bed contact time (EBCT) increased in both filters and the linear velocity (or percolation rate) decreased. The initial and final values are shown in Table 4.

Table 4: Changes in filter hydraulics as a result of changes made to feedwater flow rate in ozone pilot plant

Operating Period	GAC Filter		Sand Filter	
	EBCT (min)	Linear Velocity (m/h)	EBCT (min)	Linear Velocity (m/h)
1500 - 1900	17,1	4,9	64,4	1,1
1900 - 2500	31,2	2,5	127,5	0,5

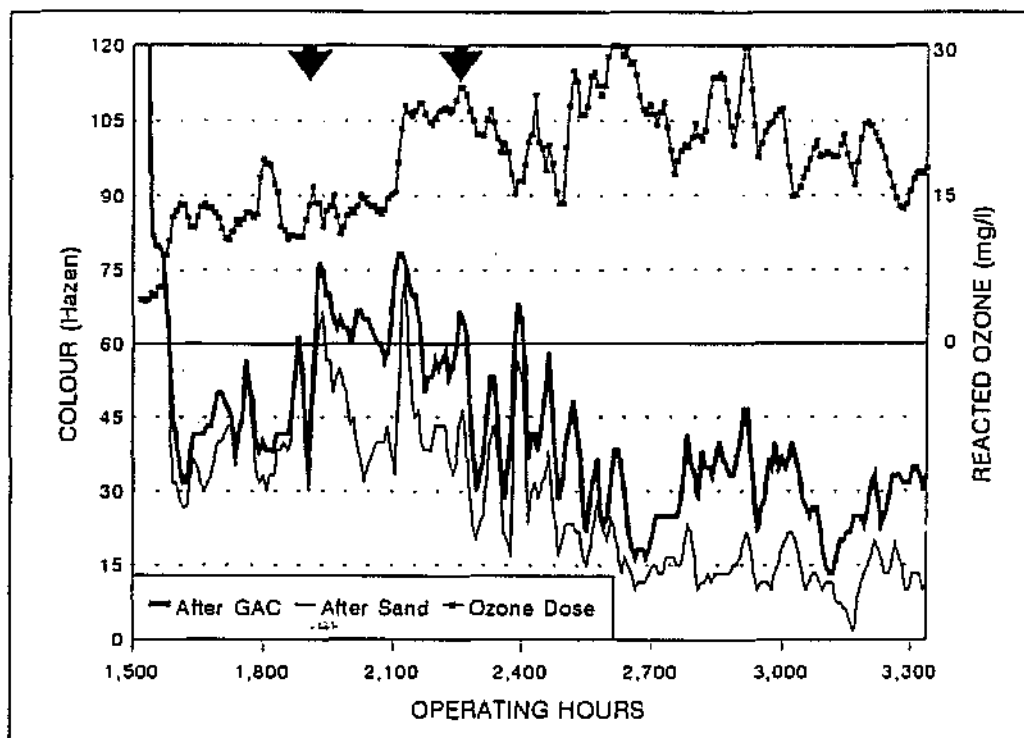


Figure 4: Variation of colour in product from filters and reacted ozone dosage

Following the backwashing incident, the sand appeared to recover more quickly than the GAC and by about 2100 hours was again achieving a water with a colour of 25 Hazen. The recovery of the GAC was slow and by 2100 had only reduced the colour of product water to about 60 Hazen.

The ozone dosage was increased to between 20 and 25 mg/l after approximately 2100 hours. This was accompanied by sharp increases in the colour of the product water from both filters, although once again the sand filter recovered quickly.

At about 2250 hours limestone chips were introduced into the feed tank to increase the alkalinity of the feed stream to the ozone contactor. The alkalinity of the water increased from approximately 17 mg/l as CaCO_3 to 25 mg/l as CaCO_3 . This

resulted in a pH increase from an average of 5,8 to 6,3. At the lower pH, the carbonic acid species dominates; whereas at the higher pH the concentration of carbonic acid and bicarbonate are roughly equal so that the increase in alkalinity would have increased the relative concentration of bicarbonate species. The reason for making this change was to observe the effect of a higher concentration of bicarbonate species on the overall colour removal process by attempting to ensure that the direct reaction pathway of the ozone dominated.

At approximately the same time that the alkalinity of the feed water was increased, nutrients in the form of fertilizer pellets were dosed into the top of each of the filters. The fertilizer contained nitrogen and phosphorus in the ratio of 2:3 by mass and did not contain potassium. About 0,1 g of fertilizer was added to each filter daily.

These changes appeared to improve the overall colour removal although the colour removal by the initial ozonation step remained fairly constant. This indicated that the rather small change in alkalinity made to the raw water was not enough to result in an improvement in colour removed by the ozonation step. Between 2600 hours and 3300 hours the sand filter produced a water with an average colour of 14 Hazen units, dropping to 10 Hazen and below on occasion. Although the product water from the GAC filter also improved, it was unable to match the quality achieved by the sand filter, and the average colour of the product water from the GAC in the last 700 hours was 30 Hazen with the lowest levels achieved being 15 Hazen.

Figure 5 shows the variation in percentage colour removal achieved after ozonation and after each of the filters.

It is clear from Figure 5 that ozonation alone was only able to achieve a removal of approximately 50 to 60 percent. Over 95 percent removal was achieved after slow sand filtration with an average of 93 percent removal in the last 700 hours of operation, and up to 90 percent after filtration through GAC.

Ozonated samples were collected from the pilot plant, prior to entering the two filters, and were filtered through filter paper in the laboratory. As expected this

improved the colour removal efficiency to about 78 percent overall. The colour removal efficiencies achieved in the GAC and sand filters indicates that filtration was not the only mechanism at work in these filters and confirms the presence of biological activity.

The sand and GAC filters were backwashed on average every third or fourth day when the pressure drop across the filter media became too high.

Two sets of water samples were analysed for THMFP, the first after 2000 hours of operation and the second after 3000 hours. Table 5 presents the results which indicate significantly lower THMFP after ozonation and filtration in both cases when compared to the raw water. The reduction in THMFP after 2000 hours was best after sand filtration at 31%. After 3000 hours the best reduction in THMFP was achieved by GAC filtration at 79%; and 61% reduction was achieved by sand filtration.

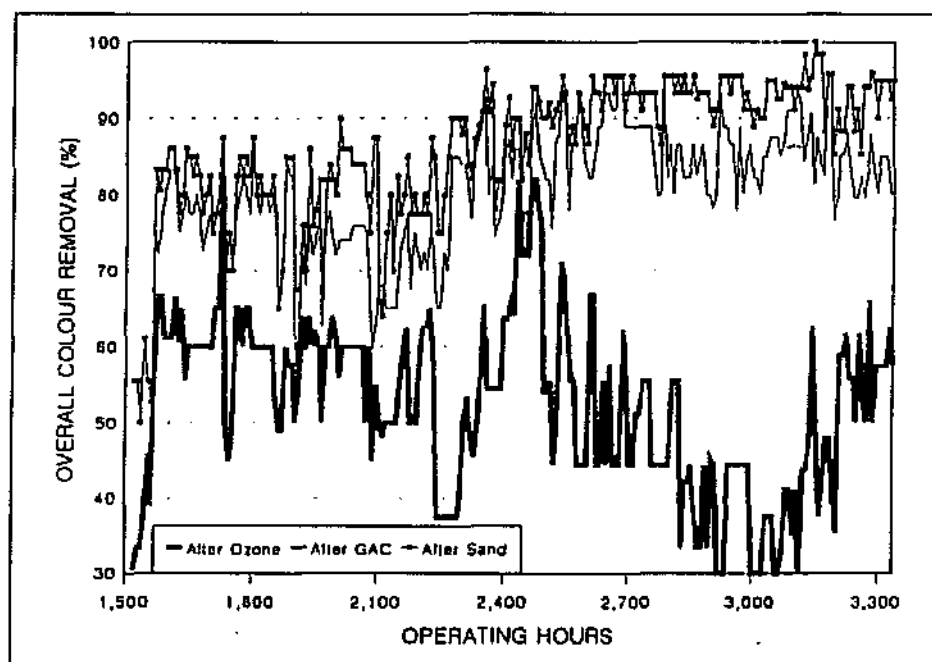


Figure 5: Overall removal of colour achieved by ozonation and after filtration through GAC and sand following ozonation

Table 5: Results of THMFP analyses carried out on the raw feed water, and ozonated water and the water produced by the two filters (12 mg/l free chlorine added) (i) = after 2000 hours; (ii) after 3000 hours

Sample		CHCl ₃ (µg/l)	CHBrCl ₂ (µg/l)	CHBrCl (µg/l)	CHBr ₃ (µg/l)	Total THMFP (µg/l)
Raw Water	i)	176	64	22	64	324
	ii)	133	61	15	53	262
After Ozonation	i)	125	65	27	95	312
	ii)	27	25	5	10	67
After GAC filter	i)	100	55	24	88	267
	ii)	19	25	11	0	55
After sand filter	i)	88	49	20	67	224
	ii)	50	31	11	9	101

After the pilot study had been completed a sample of media was obtained from each of the filters. The samples were collected from approximately 30 cm below the filter surface and in each case was inspected by a scanning electron microscopy for evidence of biological activity. Electron photomicrographs of the sand and GAC samples are shown in Figures 6 and 7, respectively. In the case of the sand no evidence of biological activity could be seen although there did appear to be significant quantities of organic debris on the sand particles.

By contrast, biological activity was evident on the GAC samples although the bacteria were not prolific. Again significant quantities of organic debris were evident. This observation raises queries as to why the sand filter performed better than the GAC filter and also why the biological activity on the GAC, at the point in the filter where the sample was taken, was rather sparse.

It was clear that in the case of the sand filter a "schmutzdecker" had formed on the surface of the sand and it is possible that all the biological activity was occurring there and very little in the bulk of the filter. The distribution of biological population in the filter was not investigated in sufficient detail to enable statements to be made on the density of these populations in the filter.

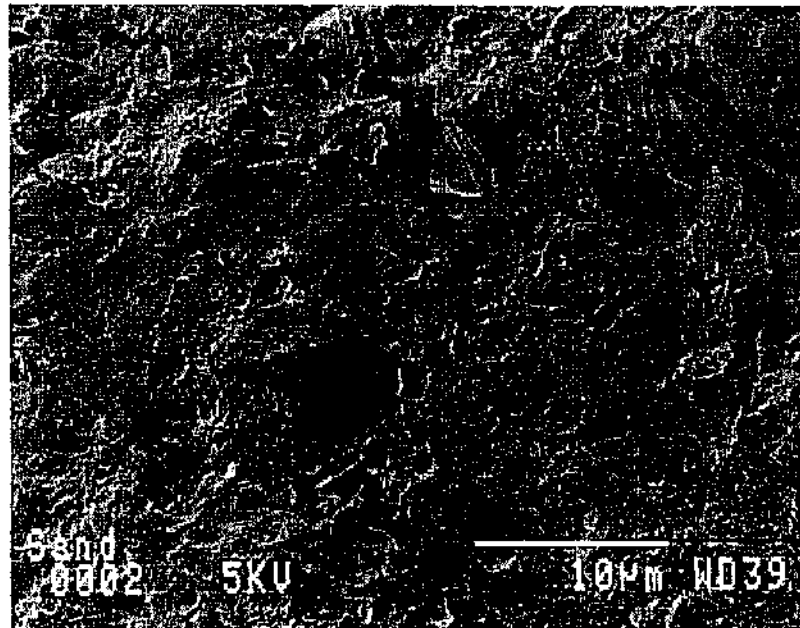


Figure 6: Electron Photomicrograph of sand sample taken 30 cm below filter surface

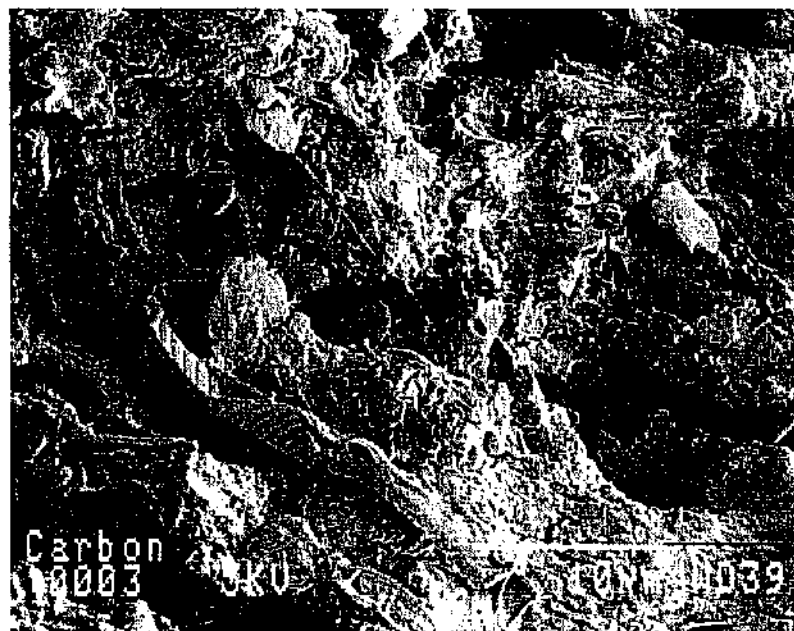


Figure 7: Electron Photomicrograph of GAC sample taken 30 cm below filter surface

3.2 MEMBRANE SEPARATION INVESTIGATION

This work was carried out in three phases; initial membrane selection, a 'semi-tech' scale continuous bench test and a continuous pilot plant study.

3.2.1 Objectives

The objectives of the investigations to remove colour using membrane separation were:

- i) To establish which membrane types were capable of removing colour during a series of selection tests on bench and continuous "semi-tech" scale.
- ii) To establish the effectiveness of selected membranes for the removal of natural colour and the degree to which fouling could be a potential problem on pilot plant scale.

3.2.2 Initial Membrane Selection

Initial membrane selections were carried out on ultrafiltration (UF) and nanofiltration (NF) membranes, using coloured water from the Duivenhoks Waterworks, in Heidelberg. Specific characteristics of the water are shown in Table 6. The purpose of the tests was to determine which of the membrane types held the most promise for colour removal and to select the best of these for pilot testing. The selection tests were carried out at two locations, Ufrotech (Johannesburg) and Membratex (Paarl).

Table 6: Quality of water from Duivenhoks river (January 1992)

	Unfiltered	Filtered
Colour (Hazen units or Pt-Co mg/l)	300	450 *
Absorbance at 545 nm	0,743	0,223
Absorbance at 275 nm	4,357	4,357
Absorbance at 254 nm	4,302	4,302

* The increase in colour is inexplicable but probably an error or a contaminated sample.

Unfortunately the Turbidity of the raw water was not recorded, but apparently it was fairly low and is estimated to have been less than 10 NTU for this particular batch of water.

a) Tests at Ufrotech

Tests on nanofiltration and ultrafiltration membranes in spiral wrap configuration were carried out at the offices of Ufrotech, the local suppliers of Osmonics membranes. The membranes used were manufactured by Osmonics in the USA. Membranes of a similar type are also available from other suppliers. The spiral wrap membranes tested and their specifications are shown in Table 7.

Table 7: Specifications of membranes tested at Ufrotech

Membrane No	Type	Material	Nominal Mol Mass Cut-off	pH range	Operating Pressure	Membrane Area (approx)
BQ 01	NF	Mod PS	400 to 500	0,5 to 13	1 400 kPa	1,9 m ²
SV 12	NF	CA	400 to 500	2 to 8	1 400 kPa	1,9 m ²
SP 12	UF	CA	500 to 600	2 to 8	750 kPa	1,9 m ²
HP 09	UF	PS	1500 to 1600	0.5 to 13	600 kPa	1,9 m ²

PS = Polysulphone C = Cellulose Acetate

b) Tests at Membratex

At Membratex in Paarl, where tubular membrane systems are manufactured, tests with 12 mm diameter tubular cellulose acetate (CA) NF membranes, (specially produced for these tests by the Institute for Polymer Science in Stellenbosch) and with polyethersulphone (PES) UF membranes, produced locally by Membratex, were carried out. The membrane types are summarised in Table 8.

Table 8: Specifications of Membranes tested at Membratex

Membrane No	Type	Material	Nominal Mol Mass Cut-off	pH range	Operating Pressure	Membrane Area (approx)
442	UF	PES	6 000	1 to 13	200 kPa	0,04 m ²
719	UF	PES	40 000	1 to 13	500 kPa	0,04 m ²
BCA 70	NF	CA	NS	3 to 8	400 to 1 000 kPa	0,04 m ²
BCA 75	NF	CA	NS	3 to 8	400 to 1 000 kPa	0,04 m ²
BCA 80	NF	CA	NS	3 to 8	400 to 1 000 kPa	0,04 m ²

NS = Not Specified

PES: Polyethersulphone

3.2.3 *Semi-technical ("semi-tech") scale continuous bench tests for colour removal*

a) Introduction

Following the initial membrane selection tests at Membratex and Ufrotech a "semi-tech" scale bench study was conducted for a period of 25 days using a modified test rig

provided by Membratex and operated with their assistance at their factory in Paarl. The purpose of this extended test was to obtain confirmation of some of the results achieved during the initial selections and also to evaluate a small UF module fitted with self-supported capillary membranes. It was anticipated that this test would also provide an indication of membrane fouling tendencies and whether effective cleaning of the membranes could readily be achieved.

b) Water used for "semi-tech" study

Six cubic metres of water was collected from the Duivenhoks river on 12 May 1992. The full analyses of the water is given in Table 1. The colour content was only 200 Hazen units. This was considerably lower than that of the water used for the initial tests, viz 300 Hazen, due to heavy rain in the area at the time the sample was collected. A disturbing aspect of this water was a high turbidity of 35 NTU which raised concerns about abnormal fouling of membranes.

c) Membranes used for "semi-tech" scale bench testing

Ultrafiltration Membranes

Three each of the Membratex, standard type 719 and 447 polyethersulphone (PES) UF membranes were operated in series in an ultrafiltration rig followed, also in series, by a standard 50 mm diameter UF module fitted with capillary PES membranes, as shown in Figure 3. The available specification for the capillary module is:

Effective membrane area	0.301 m ²
Feed inlet area	1.86 x 10 ⁻⁴ m ²
Molecular mass cut-off (Polyethylene glycol)	35 000 to 37 000

Nanofiltration Membranes

The nanofiltration (NF) test rig, which was operated in parallel with the UF rig, was used to test a "Thin film Composite" (TFC) nanofiltration spiral wrap membrane, (DESAL-5 Model 2540). The specification for this membrane is:

Molecular mass cut-off	180
Typical operating pressures	500 to 2 800 kPa
Cleaning pH range	2 to 11,5
Chlorine tolerance	2 000 mg/l - hours
2% Fructose rejection at 100 psi	98%
1 000 mg/l NaCl rejection at 100 psi	15%
1 000 mg/l MgSO ₄ rejection at 100 psi	96%

Flux was not specified, nor was the membrane area of the element known. For report purposes the output (performance) of this element is given as "Flux (l/h)". This is the total permeate flow from the element.

In series with the abovementioned spiral membrane, six tubular Cellulose Acetate (CA) nanofiltration membranes, specially produced by the Institute for Polymer Science at Stellenbosch, were also installed as shown in Figure 8. These membranes were essentially the same as the membranes used in the "Initial Tests" but from a later batch.

d) Test Rig Configuration

As mentioned above the test rig is shown in Figure 8. The UF and NF units were operated in parallel each from their own intermediate concentrate feed tanks which were, however, interconnected to allow for a degree of quality equalization. Cooling coils were fitted in these tanks to dissipate the heat produced by pumping in the recirculation loops and to maintain the temperatures at acceptable levels.

The linear velocities in the tubular UF and NF membranes were maintained at 1,5 m/s.

Overall the systems could be operated in a feed and bleed or in concentration modes as required.

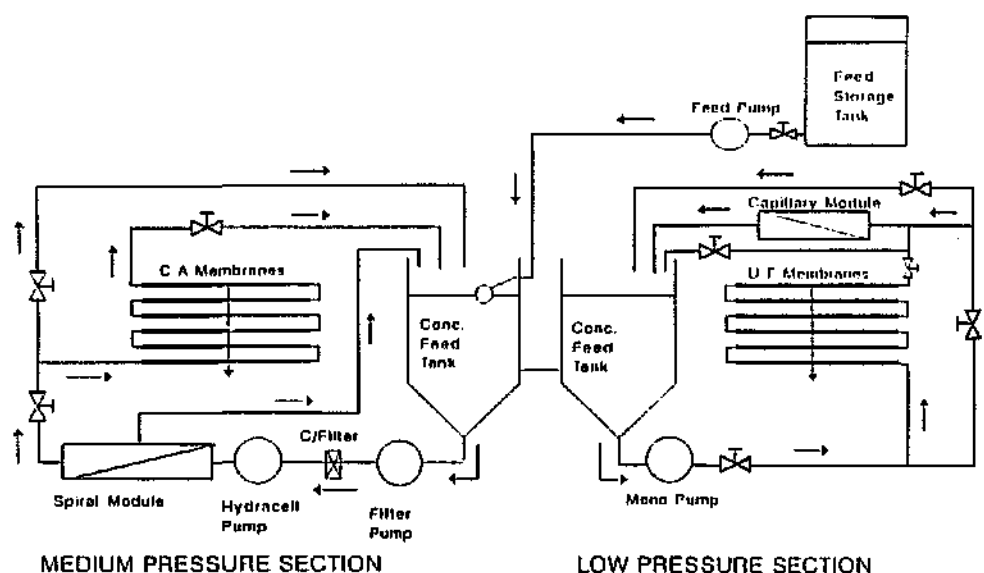


Figure 8 : Schematic of "semi-tech" membrane apparatus

3.2.4 Pilot Study

Following the laboratory experiments a membrane pilot unit was constructed. Four selected NF membrane types were incorporated into the rig, namely; an Osmonics type SV 12, (a full-fit spiral wound CA membrane); an Osmonics type BQ 01 (spiral wound PS membrane); a Desal-5 type 2540 (spiral wound TFC membrane) and a tubular CA membrane produced by the Institute of Polymer Science (IPS) in Stellenbosch.

The modules were arranged in series on the unit as shown in Figure 9 which shows the layout of the plant schematically. The modules were numbered 1 to 4 so that they could not be identified. Pretreatment of the raw feed water was provided in the form of in-line coagulation followed by pressure anthracite/sand filtration to reduce the natural turbidity of the water and membrane fouling. From the feed tank the water was pumped through two cartridge filters (nominal pore size 50 μm) and into the high pressure pump. The high pressure pump provided an operating pressure of approximately 1500 kPa. The system was operated at high levels of recirculation to simulate a plant operating at an overall water recovery of 80 percent,

which is considered to be the minimum acceptable water recovery that could be applied in practice. Under these recycle conditions the membranes received water of a quality which could be expected in the tail section of a full size plant. These operating conditions were chosen so that if membrane fouling were to be a potential problem with this water then it would manifest itself during the pilot study.

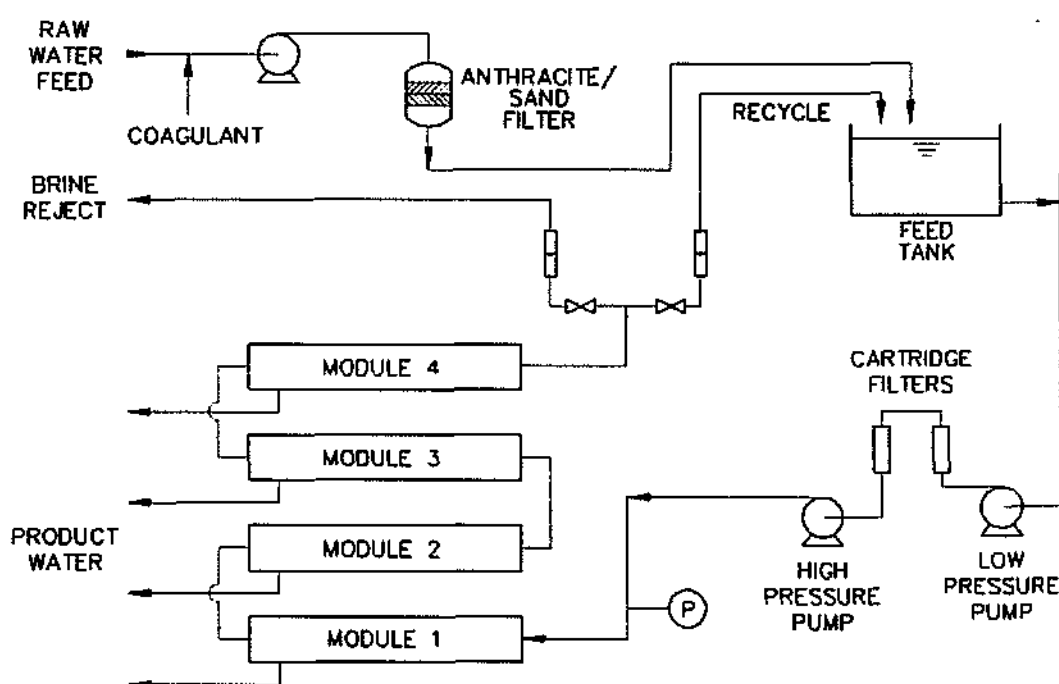


Figure 9: Schematic of membrane pilot plant arrangement

The membrane pilot unit was operated continuously and samples of feed and permeate streams were collected and analysed twice daily for colour, pH, conductivity and turbidity by the Duivenhoks staff. Measurements of permeate flow rates were made and the operating pressures within the system were recorded.

A reduction in total permeate flow rate to below the selected criterion of 75 percent of the initial permeate flow rate was taken as indicating excessive fouling and the membranes are then washed twice with a 0,2% detergent solution (Biotex).

3.2.5 Results of Membrane Separation Investigations

i) Initial Screening Tests

a) Tests at Ufrotech

The procedure adopted with each of the four candidate membranes was simply to feed the coloured water through each of them in the test rig at the appropriate pressure, with full recycle of permeate and concentrate into the feed tank. After a settling-in period of 20 minutes a permeate sample was taken for analysis. The results are shown in Table 9.

Table 9: Results of screening tests at Ufrotech

Parameter	Feed Water	Permeate (10% Recovery)			
		BQ 01	SV 12	SP 12	HP 09
Membrane type	-	NF	NF	UF	UF
pH	3,4	3,5	3,7	3,5	3,9
Conductivity (mS/m)	73,4	19,3	47,9	77,2	43,5
Colour Hazen	300	< 5	< 5	50	20

A further test was carried out at recovery levels of 50%, 75% and 90% with membrane SV 12, which was one of the two membranes that had clearly achieved the best colour removal results (down to < 5 Hazen), in the first elimination stage. In this test only the concentrate stream was recycled to the feed tank and permeate samples were taken at 50%, 75% and 90% permeate recovery levels. The results that were achieved are shown in Table 10.

Table 10: Recovery tests on SV12 membrane

Parameter	SV 12 Permeate		
	50 % Recovery	75% Recovery	90% Recovery
pH	4,5	5,7	5,7
Conductivity mS/m	15,4	17,1	18,8
Colour Hazen	10	10	<5

The results achieved clearly showed that the nanofiltration membranes were significantly more effective in achieving colour removals down to less than 5 Hazen units, than were the ultrafiltration membranes. Although the latter removed a significant amount of colour, they could not achieve the minimum required colour levels of less than 15 Hazen.

The simple experiment that was carried out to determine what results could be achieved at recovery levels of 50%, 75% and 90% indicated that the permeate colour, although slightly worse initially, improved as the recovery increased.

It was concluded that the two nanofiltration membranes BQ 01 and SV 12 would be suitable for inclusion in any further test programmes.

b) *Tests at Membratex*

In the preliminary selection tests conducted at Membratex on a standard test rig, much the same procedure was followed as at Ufrotech, except that all the membranes were tested at 90% recovery and at more than one pressure.

The results of the tests are presented in Table 11. The feed water used was the same as had been used at Ufrotech with a colour level of 300 Hazen (unfiltered) and an Absorbance (Abs) at 455 nm of 0,743.

Table 11: Results of membrane screening tests at Membratek

Membrane	Type	Pressure kPa	Flux (l/m ² .h)	Permeate Colour	545 nm
719	UF	400	143	10	0,008
442	UF	400	94	5	0,007
719	UF	700	123	5	0,005
442	UF	700	159	5	0,007
BCA 70	NF	400	23	< 5	0,006
BCA 75	NF	400	25	< 5	0,003
BCA 80	NF	400	24	< 5	0,004
BCA 70	NF	700	50	< 5	0,006
BCA 75	NF	700	59	15 *	0,037 *
BCA 80	NF	700	57	< 5	0,003
BCA 70	NF	1 000	82	< 5	0,005
BCA 75	NF	1 000	74	< 5	0,003
BCA 80	NF	1 000	90	< 5	0,006

* Poor results due to a leak

The membrane performance achieved at Membratek with the ultrafiltration and nanofiltration membranes did not differ as markedly as it had at Ufrotech. However, this was probably due to the effect of fouling on the UF membranes, which results in the formation of a dynamic membrane on the membrane surface. Dynamic membranes are known to have considerable rejection capabilities, both with respect to organic molecules and to inorganic salts, but this is usually at the expense of significant and possibly irreversible flux losses.

The nanofiltration BCA series membranes gave the best colour removal results, with product colour down to less than 5 Hazen levels.

The conclusion from the screening tests was that nanofiltration membranes should be used in preference to ultrafiltration membranes for any further test work on colour removal.

ii) "Semi-tech" Bench Scale Tests

The test was run by Membratex staff with supervision on a regular basis by Mr HA de Villiers from the Division of Water Technology in Stellenbosch. Full results are provided in Mr de Villiers's report (Annexure A to this report), and a summary of the colour parameters is given in Table 12.

Operations started on 9 June 1993 and were continued, with only short interruptions until the 3 July 1993, when the Membratex staff were required for other duties. This was unfortunate but unavoidable.

Table 12 : Summary of Analytical Data during "Semi-Tech" Scale testing of various membrane types

Date	Feed		719 UF (tubular)		442 UF (tubular)		Capillary UF		CA Tubular NF		Spiral Wrap NF		Notes
	Absorbance at 455 nm	Colour Hazen	Absorbance at 455 nm	Colour Hazen	Absorbance at 455 nm	Colour Hazen	Absorbance at 455 nm	Colour Hazen	Absorbance at 455 nm	Colour Hazen	Absorbance at 455 nm	Colour Hazen	
06.10.92	0.883	380	0.122	90	0.074	70	0.084	70	0.002	< 5	0.001	< 5	
06.11.92	0.751	450	0.115	80	0.081	70	0.131	110	0.008	< 10	0.004	< 10	
06.12.92	0.897	600	0.113	90	0.086	80	0.154	130	0.005	< 10	0.002	< 10	
06.15.92	1.215	800	0.121	80	0.095	80	0.178	150	0.013	< 10	0.002	< 10	
06.19.92	N.A.	N.A.	0.016	10	0.015	10	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	Before sponge ball clean
06.22.92	N.A.	N.A.	0.016	20	0.054	30	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	After sponge ball clean
06.23.92	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	0.012	< 5	Before NaOH pH 11.5
06.23.92	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	0.011	< 5	After NaOH pH 11.5
06.25.92	0.532	350	0.040	30	0.037	30	0.033	20	0.003	< 5	0.002	< 5	
06.26.92	0.606	350	N.A.	N.A.	N.A.	N.A.	0.028	15	N.A.	N.A.	N.A.	N.A.	
06.29.92	0.429	350	N.A.	N.A.	N.A.	N.A.	0.030	15	N.A.	N.A.	N.A.	N.A.	
07.01.92	0.584	350	N.A.	N.A.	N.A.	N.A.	0.034	15	0.012	10	0.018	< 5	
07.02.92	0.539	350	N.A.	N.A.	N.A.	N.A.	0.026	10	0.017	< 5	0.001	< 5	
07.03.92	0.505	350	N.A.	N.A.	N.A.	N.A.	0.034	15	0.008	< 5	0.001	< 5	
07.03.92	0.602	350	N.A.	N.A.	N.A.	N.A.	0.029	10	0.019	< 5	0.001	< 5	

N.A. = Not analysed

i) *719 and 442 UF Membrane*

The two tubular PES UF membranes both gave high initial fluxes of 105 and 110 litres per m² per hour (l/m².h) respectively, but within 12 hours it dropped to about 35 l/m².h and then gradually to 10 l/m².h where the flux appeared to stabilise. Sponge ball cleaning had little effect. An extensive chemical cleaning exercise with sodium hydroxide, sodium hypochlorite, Dygest 1 and 2, and with 0,5% EDTA were tried and were fairly successful, with the EDTA being the most effective. However, the flux could only be restored to 72 and 75 l/m².h for the 719 and 442 membranes respectively.

Colour removal was disappointing with residual colour variable between 10 and 90 Hazen.

ii) *Capillary Module*

The capillary module, which was operated in series with the two tubular UF membranes, had a rated clean water flux of 135 l/m².h at 200 kPa. However, this fell to 40 l/m².h after one day and gradually to 21 l/m².h after 13 days. Sponge ball cleaning cannot be done with these membranes and a similar cleaning regime as for the tubular membranes was tried, increasing the flux to 41 l/m².h. A few days later cleaning with NaOH at pH 12 for 20 minutes gave a further increase to 50 l/m².h, but this was still far removed from the initial flux of 135 l/m².h.

Colour removal initially was poor (Table 12) with residuals of 70 to 150 Hazen. After extensive cleaning colour removal improved considerably to between 10 and 20 Hazen. This was probably due to dynamic layer effects.

iii) *CA Tubular NF Membranes*

These NF membranes have a specified clean water flux of > 75 l/m².h. About 16 hours after commissioning the flux was measured at 52 l/m².h but this fell steadily to 12 l/m².h after 15 days. After cleaning it increased to 77 l/m².h but within seven days it had fallen to 22 l/m².h. Further cleaning with sodium hexametaphosphate solution (1%) raised the flux to 47 l/m².h, just before the test was stopped.

Under all conditions colour removal was very good, with colour levels of < 10 and < 5 Hazen. Absorbance at 455 nm was similar to that of the NF spiral TFC membranes (see below).

Salt rejection was between 40% and 50% on average. This is normal for NF membranes.

iv) *Spiral wrap Nanofiltration membranes*

The TFC spiral wrap element had a permeate output of 173 l/h 16 hours after it had been commissioned. This dropped fairly rapidly during the first 14 days to 30 l/h. The membrane was cleaned with NaOH solution at pH 11.4 and the output increased to 70 l/h, but dropped steadily again to 37 l/h within seven days. The membrane was then cleaned with a 1% sodium hexametaphosphate solution followed by NaOH. On recommissioning the output increased to 150 l/h and by 3 July when the tests were stopped it had risen to 167 l/h. It is believed that this improved performance could have been due to a change in the feedwater quality during the operational period mainly as a result of a marked decrease in turbidity, with a substantial proportion of the feedwater in circulation.

Colour rejection was very good, with Hazen readings below detectable limits. Absorption at 455 nm was exceptionally good; the best of the membranes tested.

The salt rejection performance of this membrane was more than 60% based on conductivity.

v) *Rejection of THM-precursors by nanofiltration membranes*

The THMFP was determined by chlorinating (12 mg/l for 12 hours) the feed to the two nanofiltration systems (CA tubular and TFC spiral) and their respective permeates and determining the THMs that had been formed. The results are presented in Table 13.

Table 13 : Trihalomethane Formation Potential Determination of raw feedwater and permeate samples

THM	Feed (mg/l) 15 June	CA Tubular NF		Spiral TFC NF	
		Permeate (mg/l) 15 June	Permeate (mg/l) 3 July	Permeate (mg/l) 15 June	Permeate (mg/l) 3 July
CHCl ₃	190	27	29	19	23
CHBr-Cl ₂	25	23	16	16	4
CHBr ₂ -Cl	0	9	6	6	2
CHBr ₃	10	5	1	4	3
Total	225	64	52	45	32

The THMPF of the feedwater amounted to 233 µg/l. Totals of 64 µg/l and 52 µg/l for the CA Tubular membrane and 45 µg/l and 32 µg/l for the TFC spiral membrane on the two days that samples were taken. These results indicate the good potential that the NF membranes have for the reduction of the THMPF.

iii) *Pilot Plant Study*

The membrane pilot plant, fitted with four types of NF membranes selected from the screening tests (three in the spiral configuration and one in the tubular configuration), operated for approximately 900 hours at the Duivenhoks Works. Unfortunately the high pressure feed pump was unreliable and as a result the operating time was limited.

Nevertheless sufficient data was gathered within the operating period to establish the technical viability of this process for removal of colour.

The plant was operated in continuous recycle mode in order to concentrate the colour and expose the membranes to conditions that could be expected to occur in the tail end of a plant operating at approximately 80 percent water recovery. Therefore while the raw feed water colour varied between 200 and 250 Hazen, the average colour of the feed stream to the modules during the present experimental period varied between 400 and 600 Hazen.

The extent to which the four membranes individually removed colour from the water can be seen from Figure 10 in which the colour of the permeate streams from each module,

is plotted. Module 2 produced the poorest quality water with colour levels reaching 100 Hazen at one point. Initially the colour of the permeate from this membrane was good, being below 5 Hazen for the first 100 hours. Module 1 also started off well but after 400 hours excursions to around the 20 Hazen level became fairly frequent. Module 4 performed well throughout the operating period as far as colour removal is concerned, one excursion to 40 Hazen units at approximately 700 hours could have been a sampling error. The best colour removal, however, was achieved by Module 3 with a permeate colour of zero Hazen for most of the operating period.

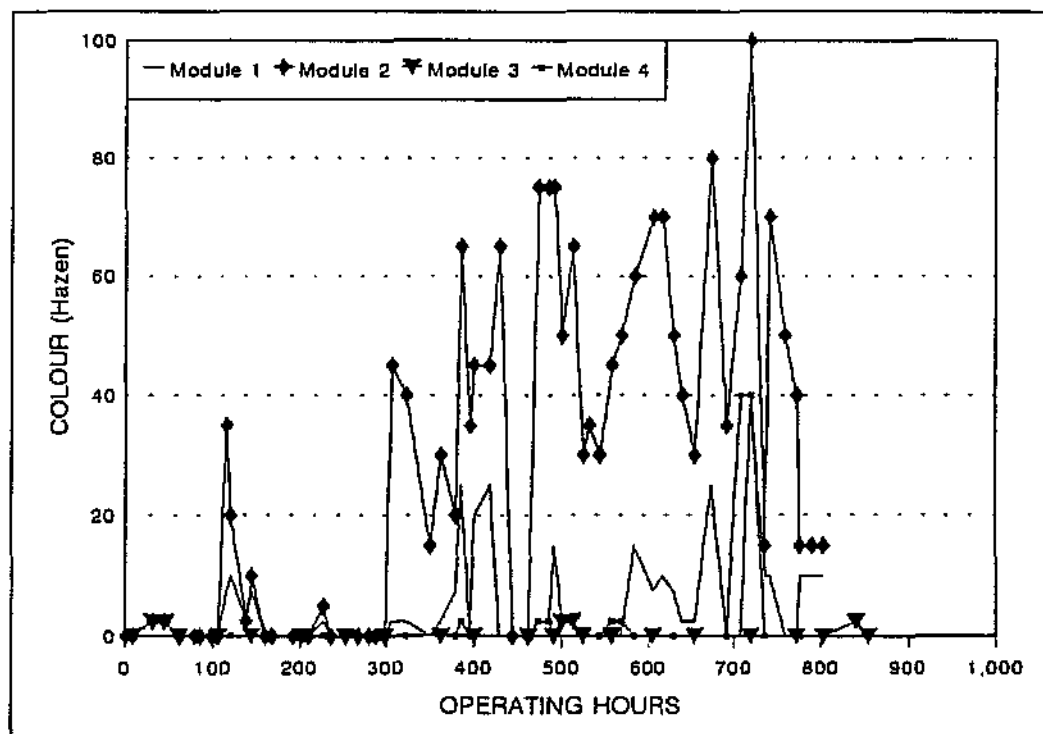


Figure 10: Colour levels of the product water from the four membrane modules during the 900 hours of the pilot study

Although good colour removal is necessary it is not the only important parameter that requires consideration in membrane systems; product output or flux is also critical. Measurements of the permeate flowrate from each of the four membrane modules were taken twice daily. The variation in pressure drop across the membrane modules

remained fairly constant throughout the study at between 200 and 300 kPa. Although there were problems with the high pressure feed pump an average feed pressure of about 1500 kPa was maintained for most of the period. The temperature of the feed water did not vary much during the study and averaged about 20°C.

Exact values of flux corrected for temperature and pressure have not been reported. The objective was to observe changes in actual output as being indicative of membrane fouling and the operating conditions for all four modules were virtually the same. Figure 11 shows the variation in permeate production from the four membrane modules for the operating period. As can be seen there was significant variation in the permeate flowrate from each of the membranes. After the first 100 hours of operation the total permeate flowrate had dropped to less than 75 percent of the initial output and it was obvious that serious fouling was taking place.

In order to restore the permeate output the membranes were washed twice with a 0,2% (m/m) Biotex detergent solution. This is indicated by an arrow at 100 hours (Figure 11). The recovery in permeate flowrate can be seen and it is evident that Biotex flushing is a very effective foulant dispersant. However, within an unacceptably short time the overall permeate flowrate had dropped again and further washing was required. The arrows in Figure 11 indicate how frequently membrane washing was necessary; approximately every 50 hours.

The cause of the rapid fouling of the membranes was almost certainly the variable turbidity of the raw feed water (5 to 20 NTU) and in-line coagulation/filtration was introduced in an attempt to reduce the turbidity to acceptable levels. Figure 12 shows the variation of turbidity in the raw feed stream and in the feed stream entering the modules. Toward the end of the operating period some instances of very high turbidity were encountered (greater than 80 NTU). However, a worrying factor was that the in-line coagulation and filtration to reduce the turbidity had little effect. Coagulants that were tried were alum and a (polyaluminium chloride) PAC polyelectrolyte blend.

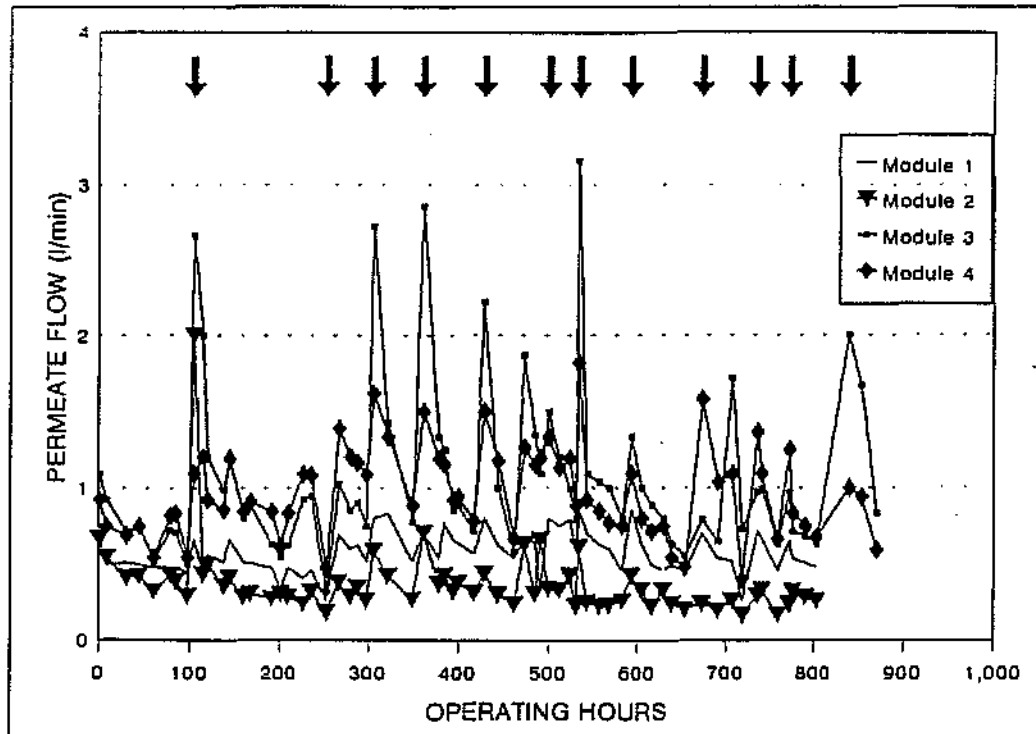


Figure 11: Variation in permeate flowrate from the membranes

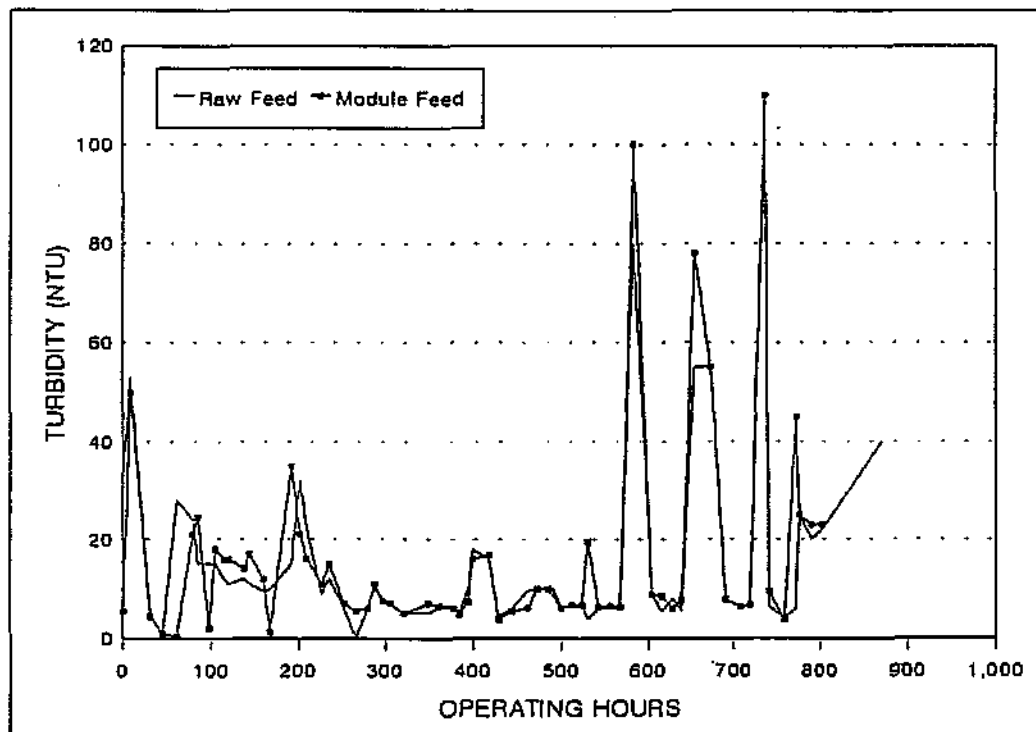


Figure 12: Variation of turbidity of raw feed and pretreated feed water to the pilot plant

3.3 Effectiveness of conventional colour removal processes

3.3.1 Objective and Method

The objective of this section of the experimental work was to provide comparative data on the colour removal efficiencies and reduction in THMFP, between the ozonation and membrane separation process, and the conventional colour removal processes used in the Southern and Western Cape areas.

To meet this objective water samples were collected from four different waterworks and analysed. Samples of both the raw water and the final product water were collected from the four plants and all samples were analysed for colour the residual THM concentration and the THMFP.

3.3.2 Findings

The plant performance data, obtained from four treatment works is presented in Table 14. In order to preserve the identity of the works they are referred to as Plants A, B, C and D.

The only information of interest to this investigation was the method of treatment used, the colour of the raw and product water, the THM concentrations of the final chlorinated treated water and the THMFP of the treated water.

Table 14: Summary of plant and performance data from four conventional water works treating brown waters

Plant	Colour Removal Method Used	Raw Water Colour (Hazen)	Treated Water		
			Colour (Hazen)	THM ($\mu\text{g/l}$)	THMFP ($\mu\text{g/l}$)
A	Ferric Sulphate Lime	70	< 5	53	149
B	Alum Lime	400	< 5	18	105
C	Alum Lime	200	< 5	53	109
D	Alum, Sodium, Aluminate Lime	150	< 5	45	96

* THMFP analytical procedure:

12 mg/l Cl_2 dosage and analysis after 14 hours.

It is evident from the table that the colour of the raw feed water to the four plants varies considerably, from 70 Hazen for Plant A to 400 Hazen for Plant B. Despite this, the colour of the treated water produced at each plant was less than 5 Hazen units. All four plants use the coagulation method for clarification and colour removal, but the type of coagulant and/or combination of coagulant(s) varies as shown.

The THM concentrations in the treated water (after the normal process of final disinfection with chlorine prior to discharge to the distribution system) show that all of the plants produced THMs in their water, but that these were all below 60 $\mu\text{g/l}$. This can be compared with the new THM regulations in the USA which have reduced the maximum allowable concentration of THMs in potable water from 100 $\mu\text{g/l}$ to 80 $\mu\text{g/l}$.

It is clear from the high THMFP results in the table that the concentration of THMs in the treated water would be significantly greater in all cases if more chlorine was added to the water or the contact time increased. The THMFP reported in the table was obtained after a dosage of 12 mg/l of chlorine was added to each sample and the THM analysis carried out 14 hours later.

A comparison of the results obtained from the four conventional plants, and those from the pilot plant investigations, is made in the next section.

4. DISCUSSION

4.1 Ozonation

The initial laboratory test work showed that by the addition of ozone alone a substantial proportion of the colour could be removed from the water. However, even at very high dosages (71 mg/l) it was not possible to remove the colour to acceptable levels even with extended contact times in the reactor. Colour removal efficiencies of up to 95 percent were achieved after filtering (through 0,45 μ m filters) the ozonated product water. Without filtering colour removal efficiencies of up to 85 percent were achieved. The best final colour achieved was 10 Hazen units.

The inability of the ozone to remove all colour is in line with the findings of other workers (Tan and Amy, 1991; Ødegaard *et al*, 1986). In recent work van der Walt (1993) reports almost complete colour removal from laboratory prepared waters to which humic acids were added to produce a colour of 300 mg/l Pt-Co, with ozone dosages of only 14 mg/l. This illustrates the significant differences that can be obtained when working with synthetic and real waters.

High removal of colour tended to be accompanied by a high reduction in UV absorbance at 254 nm. This is indicative of the fact that the molecules responsible for colour contain double bonds, which are attacked by ozone.

The influence of hydrogen peroxide and ozone on the removal of colour was variable, being best at a hydrogen peroxide dose to ozone reacted concentration ratio of 1:1,9. However, high ozone reacted concentrations on their own removed more colour. As expected the presence of hydrogen peroxide improved the efficiency of ozone transfer as a result of the affinity between ozone and hydrogen peroxide which allows less ozone to escape unreacted.

The laboratory study also showed that increasing the hydraulic retention time in the contact column improved colour removal.

The results achieved with the pilot study have indicated that biological action in both GAC and sand filters probably became significant after approximately 1500 hours

(2 months) of operation. However, for practical reasons this could not be established by means of total plate counts, ATP analysis or regular electron microscope investigations.

The 20 to 25 mg/l reacted dosage of ozone applied after about 2 000 hours was equivalent to a dosage of 1,5 mgO₃/mg TOC which is within the range quoted in the literature by Singer (1990) to produce optimum biodegradability of the water.

No explanation can as yet be offered as to why the sand filter performed better than the GAC filter, other than that the loss of part of the GAC at approximately 1900 hours could in some way have been responsible. However, the plant operated for a further 1400 hours and although the GAC filter's performance improved, it did not match that of the sand filter.

The significant improvement in the performance of both biological filters after the implementation of nutrient addition to the filters does indicate that in systems where the biodegradable fraction of the DOC could be large that nutrient deficiency could be a limiting factor. The biodegradable DOC (BDOC) was not measured during the test work, however the high DOC of the raw water (12 mg/l) indicates that the BDOC could also be high and therefore the natural nutrient content of the water could become the limiting nutrient during the aerobic biological oxidation. The significance of this would need to be evaluated during further work which is discussed later.

During the period following the addition of nutrients (notwithstanding the crude method that was used) the reduction in the THMFP of the product water also improved. In the two analyses that were carried out the THMFP after ozonation and the GAC filter was 55 µg/l, while that after ozonation and the sand filter was 101 µg/l. These values are both lower than the THMFP measured at four treatment plants using the conventional coagulation methods for colour removal (the exception was plant D which had a THMFP of 96 µg/l slightly less than that produced by the biological sand filter).

Bearing in mind that the ozonation plus biological filtration process was able to reduce the colour content of the water to below 10 Hazen, indicates that in a more optimized system colour levels of less than 5 Hazen could conceivably be achieved continuously.

In such a situation the reduction in the THMFP by this process could be even more significant than the results achieved in the pilot study, when compared with conventional coagulation treatment methods.

4.2 Membrane Separation

It is apparent from the results achieved with the relatively short pilot plant investigation that nanofiltration membranes, whether of the Thin Film Composite type or of asymmetric cellulose acetate type, would be suitable for colour removal from typical southern Cape waters. However, membrane fouling was found to be to be a problem at the Duivenhoks site. The turbidity of the water (as received) used during this test was high at up to 35 NTU. This is excessive and probably largely responsible for the serious flux declines experienced.

It should also be remembered, when comparing THMFP results, that the method used for analysing the samples presented in this report is not the seven day residual method used internationally (specifically in the USA) where the chlorine demand of the sample is estimated prior to the chlorine dose being applied. Therefore comparison of THMFP results reported here with results obtained during overseas work should be made with caution.

Disappointingly the only pretreatment method tried namely inline coagulation/ filtration through a dual media (anthracite/sand) filter has not been effective and this requires further study. Whatever method is used it has to be simple and inexpensive, because if not, the membrane separation process would not be competitive.

Two of the four nanofiltration membrane systems tested, were able to achieve good to excellent colour removals over the test period. However, all membranes were prone to severe fouling, necessitating unacceptably frequent membrane cleaning operations. In practice this would result in plant down-time and cleaning material costs, but fortunately the cleaning appears to be very effective.

THM-precursor removed by the nanofiltration membranes has also been shown to be good and holds promise for excellent quality of water treated by this process. The THMFP in the product water produced by the two membranes that performed the best

during the pilot trial were all less than 65 $\mu\text{g/l}$. This shows that the NF membrane process, as expected, is capable of reducing the THMFP of the product water to concentrations well below those produced by the conventional coagulation processes. In the samples from four conventional plants the THMFP in the product water varied between 96 and 149 $\mu\text{g/l}$.

The pilot study has given a clear indication that under the conditions prevailing at Duivenhoks the nanofiltration membranes can achieve good colour removal at 80 percent recovery levels.

Advantages of the membrane process are seen to be its compact size, the elimination of the major problem of sludge disposal and the effective reduction in trihalomethane precursors.

A probable disadvantage is that at best the recovery of decolourised water can only be about 95% possibly as low as 90%. The result of this is a concentrated stream of high colour at least ten times more intense than that of the feedwater to the plant. Disposal of this water into the stream from which the water is drawn is possible, but problematic, unless of course the discharge can be made into the mouth of the river, where it discharges into the sea or by relatively small pipeline directly into the sea or a large lagoon.

5. PRELIMINARY ESTIMATES OF CAPITAL AND OPERATING COSTS FOR FULL SCALE INSTALLATIONS

It should be noted that although the costs presented in this section are comparable, they do not represent the complete cost of a water treatment facility, since the operations of stabilization and disinfection (which are common to all have been excluded).

Both capital and operating cost approximations are presented for each option. The Nett present value (NPV) analysis was carried out over a 20 year period for various nett interest rates between zero and 8 percent. From the NPV costs an overall estimate of the unit cost (expressed as c/m³ of water produced) was made, from which the costs of the various options can be compared.

5.1 Ozonation

Based upon the findings of the laboratory study and the pilot plant investigation three capital cost estimates have been made. The first is for a direct ozonation system based on the dosages established in the laboratory study. The second and third are for ozonation followed by either GAC or sand filters operating in the biological mode in accordance with the pilot plant investigation.

5.1.1 *Direct Ozonation Only*

Based on the preliminary findings discussed above and the type of ozone transfer efficiencies quoted in the literature for full scale plants, the following parameters were used as a conservative basis for costing.

Efficiency of ozone transfer:	90%
Ozone reacted concentration required:	70 mg/l
Ozone dosage (calculated):	78 mg/l
Raw water treatment capacity:	5 300 m ³ /d
Ozonation treatment capacity:	5 150 m ³ /d
Sand filter treatment capacity:	5 150 m ³ /d
Plant availability:	90%

Pretreatment would include microscreening to remove the bulk of the suspended material and post treatment would include pressure sand filtration to remove any remaining solids and microflocs formed in the ozonation process. The budget capital costs are presented in Table 15. It is assumed that the plant would be constructed on an existing site and that no additional water storage would have to be provided. The estimated capital cost is R8,94 million (excluding VAT) . The operating costs for the ozonation installation are summarised in Table 16 and total R881 000 per annum.

The results of the NPV analysis on this option are in the cost summary section, Section 5.4 on page 58.

Table 15: Budget Capital Costs for Ozonation Installation to produce 4 500 m³/d of product water

Description	Budget	Cost
	Civils R(000)	Mechanical and Electrical R(000)
Fine screens (5 300 m ³ /d)	50	200
Ozonator complete (420 kg/d)	500	4 500
Contactors	100	900
Ozone destructor	50	200
Buildings (100 m ²)	60	
Sand filters (4 800 m ³ /d)	50	200
Electrical supply		200
Sub Total 1	810	6 200
Allowed for P&G on Civils	162	
Allow for Engineering	97	620
Allow for Contingencies	122	930
Sub Total 2	1 191	7 750
GROSS TOTAL (EXCLUDING VAT)	8 941	

Table 16: Summary of operating costs for a 4 500 m³/d ozonation installation

Description	Annual Cost R
Ozone Production (R2,5 /kg)	380 000
Labour	174 000
Coagulant for filtration (5 mg/l)	9 000
Maintenance 1% of nett civil costs	8 000
Maintenance 5% of nett mechanical costs	310 000
TOTAL ANNUAL	881 000

5.1.2 *Ozonation plus biological treatment in GAC*

Using the results obtained during the study, the following parameters were used as a conservative basis for sizing the ozonator and GAC filter.

Efficiency of ozone transfer:	90%
Ozone reacted concentration required:	20 mg/l
Ozone dosage (calculated):	22 mg/l
Raw water treatment capacity:	5 300 m ³ /d
Ozonation treatment capacity:	5 150 m ³ /d
GAC filter treatment capacity:	5 150 m ³ /d
Plant Availability:	90%

As for the first option, pretreatment would involve fine screening to remove the bulk of the large suspended material. The GAC filters were sized for a conservative down flow velocity of 10 m/h, an empty bed contact time of 10 minutes and a column depth of 2 m. This gives a total GAC requirement of approximately 50 m³. The GAC could also act as the final filtration step as well. It is assumed that the GAC would be replaced every three years although this may not be necessary as the adsorptive capacity of the carbon is not critical in this application and therefore only partial regeneration may be required.

The capital costs for this option are shown in Table 17, with the operating costs in Table 18. The total estimated capital cost is R5,401 million (excluding VAT). The annual operating cost amounts to R565 000.

Table 17: Budget Capital Costs for Ozonation followed by biological GAC filters to produce 4 500 m³/d of product water

Description	Budget	Cost
	Civils R(000)	Mechanical and Electrical R(000)
Fine screens (5 300 m ³ /d)	50	200
Ozonator complete (120 kg/d)	300	1 500
Contactors and destructor	100	900
Buildings (100 m ²)	60	
GAC filters (5 150 m ³ /d)	400	550
Electrical supply		100
Sub Total 1	910	3 250
Allow for P&Gs on Civils	182	
Allow for Engineering	109	325
Allow for Contingencies	137	488
Sub Total 2	1 338	4 063
GROSS TOTAL (EXCLUDING VAT)	5 401	

Table 18: Summary of operating costs for a 4 500 m³/d ozonation and biological GAC filtration installation

Description	Annual Cost R
Ozone Production (R2,5 /kg)	110 000
Labour	174 000
Replace GAC every three years	100 000
Coagulant for filtration (5 mg/l)	9 000
Maintenance 1% of nett civil costs	9 000
Maintenance 5% of nett mechanical costs	163 000
TOTAL ANNUAL	565 000

5.1.3

Ozonation plus biological treatment in sand filters

This option is similar to the previous one except that the GAC filters are replaced with sand filters. The requirements for the ozonator will not change. Based upon the experience of the pilot plant investigation the downflow velocity through the sand was set at 1 m/h for this cost exercise, with an empty bed contact time of 15 minutes.

With the above design criteria the area requirements of the sand filters would be over 200 m².

The capital cost of such a slow sand filter installation is expected to have a civil component of R80 000 and a mechanical/electrical component of about R50 000. These costs are shown in Table 19, and total R5,614 million (excluding VAT).

Table 19: Budget Capital Costs for Ozonation followed by biological sand filters to produce 4 500 m³/d of product water

Description	Budget	Cost
	Civils R(000)	Mechanical and Electrical R(000)
Fine screens (5 300 m ³ /d)	50	200
Ozonator complete (120 kg/d)	300	1 500
Contactors and destructor	100	900
Buildings (100 m ²)	60	550
Sand filters (5 150 m ³ /d)	800	250
Electrical supply		100
Sub Total 1	1 310	2 950
Allow for P&G on Civils	262	
Allow for Engineering	157	295
Allow for Contingencies	197	443
Sub Total 2	1 926	3 688
GROSS TOTAL (EXCLUDING VAT)	5 614	

Table 20: Summary of operating costs for a 4 500 m³/d ozonation and biological sand filtration installation

Description	Annual Cost R
Ozone Production (R2,5 /kg)	110 000
Labour	174 000
Coagulant for filtration (5 mg/l)	9 000
Maintenance 1% of nett civil costs	13 000
Maintenance 5% of nett mechanical costs	148 000
TOTAL ANNUAL	454 000

The operating costs are as per the previous option except that no provision has been made to replace the sand, since it will be possible to backwash the filters periodically to remove excess biomass and suspended solids or to clean the filters manually by removing the top layer of sand.

The annual operating costs amount to R454 000 and are shown in Table 20.

Bearing in mind that the best performance from the sand filter during the pilot study was when the filtration velocity was only 0,5 m/h, the filtration area allowed for the above may not be conservative enough in practice. This should be taken into account when comparing costs. Reducing the filtration rate to 0,5 m/h would increase the capital cost of the option by about R800 000.

5.2 Membrane Separation

Using a similar conservative approach as was used for costing the ozonation process options, a membrane separation plant using spiral wrap nanofiltration membranes was costed.

The capital costs are summarise in Table 21 and are for a plant based upon the results obtained in the pilot plant study. As indicated the estimated total capital cost is R7,735 million (excluding VAT).

The estimated operating costs for such a plant are shown in Table 22. The power consumption was assumed to be for a plant with interstage pumping, and membrane life was assumed to be three years. The total annual operating costs are estimated to be R1,048 million.

Table 21: Budget Capital Costs of a Nanofiltration Installation to produce 4 500 m³/d of product water

Description	Budget Cost	
	Civils R(000)	Mechanical and Electrical R(000)
Feed water pretreatment	500	100
Nanofiltration plant with membranes	50	5 000
Buildings (200 m ²)	120	
Electrical Supply		200
Sub Total 1	670	5 400
Allow for P&G on Civils	134	
Allow for Engineering	80	540
Allow for Contingencies	101	810
Sub Total 2	985	6 750
GROSS TOTAL (EXCLUDING VAT)	7 735	

Table 22: Summary of operating costs for a 4 500 m³/d membrane nanofiltration installation

Description	Annual Cost R
Labour	174 000
Chemicals for pretreatment plant	50 000
Energy Cost (@ 10c/kWh)	190 000
Membrane Replacement (3 yearly)	417 000
Maintenance 1% of nett civil costs	7 000
Maintenance 5% of nett mechanical costs (excluding membranes)	210 000
TOTAL ANNUAL OPERATING COST	1 048 000

5.3

Conventional Alum Dosing followed by sedimentation

To bring the capital and operating costs for the ozonation options and membrane filtration options into perspective with the cost of a conventional treatment method for colour removal, a cost estimate has been carried out for an alum coagulation/flocculation and sedimentation installation to produce 4 500 m³/d of decolourised water.

The costs are based on recently installed installations of this type in the Cape area, and are presented in Table 23. The capital cost amounts to R6,365 million (excluding VAT). The operating costs are presented in Table 24 and are based upon an alum dosage of 100 mg/l which is usual for a raw feed water of about 200 Hazen units.

Labour requirements were assumed to be the same as those for the other options presented above. The total annual operating cost is estimated to be R589 000.

Table 23: Estimated capital cost for conventional alum coagulation and sedimentation plant to produce 4 500 m³/d of product

Description	Budget	Cost
	Civils R(000)	Mechanical and Electrical R(000)
Coarse screening	60	60
Chemical Dosing System	100	400
Coagulation System	400	200
Sedimentation	1 000	750
Final Filtration	800	200
Sludge Transfer and Disposal System	430	150
Electrical Supply		50
Sub Total 1	2 790	1 810
Allow for P&G on Civils	558	
Allow for Engineering	335	181
Allow for Contingency	419	272
Sub Total 2	4 102	2 263
TOTAL ESTIMATED CAPITAL COST	6 365	

Table 24: Summary of operating costs for conventional alum coagulation and sedimentation plant to produce 4 500 m³/d of product water

Description	Annual Cost (R)
Labour	174 000
Chemicals (Alum, polymer, lime)	296 000
Maintenance 1% of nett unit cost	28 000
Maintenance 5% of nett mechanical cost	91 000
TOTAL ANNUAL OPERATING COSTS	589 000

5.4

Cost Summary

The capital and operating cost options presented in this section are summarised in Table 25. The reference unit cost of product water from each of the processes was calculated at various nett discount rates, using the cost information/ The results of the NPV analyses in terms of the reference unit costs of producing product water are presented in Table 26. The civil costs were based on a life of 20 years, and the mechanical costs on a life of 15 years, for the total 20 year period.

The results show that for any positive nett discount rate, the option of ozonation followed by biologically enhanced sand filtration or GAC filters is the cheapest - being about 5 percent less than the conventional alum coagulation method, with a product reference unit cost of between 66 and 85 c/m³ for the GAC system and up to 14 percent less for the sand option (between 60 and 79 c/m³ product). On the other hand, direct ozonation and membrane nanofiltration could be about 55 percent more costly than the conventional alum treatment method, at costs of between 108 and 142 c/m³ of product water.

Table 25: Summary of capital and operating unit costs for various process options to remove colour

Process Option	Estimated Capital Cost R (million)	Annual Operations Cost R (000)
Direct Ozonation	8,94	881
Ozonation plus biological GAC	5,40	565
Ozonation plus biological sand filters	5,61	454
Membrane Nanofiltration	7,74	1048
Conventional Alum Coagulation	6,37	589

Table 26: Summary of NPV analysis of colour removal options over a 20 year life cycle at various nett discount rates

Process Option	Reference Unit Cost of Nett Discount Rates (c/m ³)				
	0%	2%	4%	6%	8%
Direct Ozonation	118	108	118	128	140
Ozonation plus biological GAC	71	66	72	78	85
Ozonation plus biological sand filters	63	60	66	72	79
Membrane Nanofiltration	123	115	123	132	142
Conventional Alum Coagulation	68	69	75	82	90

6. CONCLUSIONS

6.1 Ozonation

6.1.1 Direct ozonation was capable of removing up to 95 percent of the colour in a water sample with a colour content of 200 Hazen, after filtration of the ozonated sample. The best product water achieved during the ozonation test work had a colour of 10 Hazen at a reacted ozone dosage of between 50 and 70 mg/l.

6.1.2 Direct ozonation was able to reduce the UV absorbency of the water at 254 nm in direct relation to the final colour content of the water.

6.1.3 The removal of colour by a mixture of hydrogen peroxide and ozone was generally not as effective as with the same concentration of ozone on its own.

6.1.4 Direct ozonation was able to reduce the concentration of THMs that were formed in the product water after the addition of 12 mg/l of free chlorine for a 12 hour period. This is interpreted as a reduction in the concentration of THM precursors in the water.

6.1.5 Ozonation followed by biologically enhanced GAC and sand filters was able to achieve up to 90 percent removal and 95 percent colour removal respectively at an average reacted ozone dosage of 22 mg/l.

Product water leaving the sand filter had an average colour content of 14 Hazen during the last 700 hours of the pilot study. This was low enough to meet the SABS recommended limit of 20 Hazen. The average colour content of the water from the GAC filter during this period was 30 Hazen. The reasons for the poorer performance of the GAC filter are not clear.

6.1.6 Introduction of a small quantity of the nutrients nitrogen and phosphorus to the feed water entering the two biologically active filters appeared to have a significant impact on improving the performance of the process and reducing the colour content of the filter product waters.

6.1.7 Preliminary cost estimates have shown that the combined process of ozonation followed by biologically enhanced filtration at a reacted ozone dosage of about 20 mg/l is cost competitive with the conventional alum coagulation process and is expected to be between 5 and 14 percent cheaper, based on a 20 year NPV analysis of capital and operating costs.

6.1.8 Based upon the findings of the investigation the further development of the ozonation plus biologically enhanced filtration process for the removal of highly coloured waters appears to have considerable merit.

However, before this process can be recommended for commercial scale application further process investigations are necessary, aimed at optimising the performance of both the ozonation section of the process and the biological filtration section. Proposals for future work are presented in Section 7.

6.2 Membrane Separation

6.2.1 The investigations indicated quite clearly that nanofiltration membranes are superior to ultrafiltration membranes for the removal of natural colour from Cape waters.

6.2.2 The nanofiltration membranes chosen for the pilot plant instigation were able to achieve better colour removal efficiencies than ozonation, the best two membranes producing product water with colour values of less than 5 Hazen units.

6.2.3 Nanofiltration is a technically viable option for colour removal of humic/fulvic type waters at the 80 percent recovery levels, but even higher recoveries can probably be achieved.

6.2.4 Membrane fouling was a problem. Fortunately the foulants did not appear to be bound irreversibly to the membrane and cleaning was effective. The reason for the fouling was probably mainly due to the relatively high turbidity of the feed water to the pilot unit.

There can be no question about the practicability of pretreatment to remove the fouling but this needs to be very inexpensive process, in order to ensure the economic viability of the membrane colour removal process.

6.2.5 Preliminary indications are that the cost of nanofiltration membrane separation for colour removal could be about 55% above that of conventional metal salt coagulation treatment processes. Less if membranes should last five or even more years.

The implications for further work are discussed in Section 7.

7. DISCUSSION AND PROPOSALS FOR FURTHER WORK

7.1 Background

A Workshop on natural organic matter (NOM) which was held between 19 and 23 September 1993 in Chamonix, France was attended. Also in attendance were several personalities from well-known academic institutions in the USA who have been involved with colour removal studies using ozone and membranes as reported in the literature. NOM includes natural colour in water and the following important points relating to the treatment and removal of NOM from water were discussed at the Workshop.

- i) The fouling of membranes by NOM is a worldwide problem for which the solutions are not known. A research project to be funded by the American Water Works Association Research Foundation (AWWARF) was proposed to look into the mechanism by which fouling of membranes by NOM takes place. This would include investigations into the effects of membrane physical/chemical properties hydrophobicity on the fouling phenomenon.
- ii) Although ozonation of water to remove colour has been carried out in several places, particularly on waters with relatively low colours (less than 100 Hazen); the combination of ozonation followed by biologically enhanced filtration has not been used for treating coloured water. The participants at the workshop showed great interest in the pilot study that was done at Duivenhoks. In addition there are presently two AWWARF projects underway in the USA investigating the optimisation of biologically enhanced GAC filtration for NOM removal. Although this work is aimed at waters with considerably lower DOC concentrations than those of the Cape, the information from both of these studies is expected to be relevant to any further work carried out in South Africa in this area of application.

7.2

Proposal for further work

Based upon the findings of the pilot plant investigations using the ozonation techniques and the membrane separation methods, the expected costs of the various treatment options, the discussions with overseas peers in this field, and the direction of overseas research, it is proposed that further work be carried out on the combination of ozonation followed by biologically enhanced filtration. This process has shown considerable potential during the pilot study and the possible cost savings that could be achieved relative to the conventional treatment method provide further incentive for continued investigations.

The fouling aspects associated with the membrane process would be where any further work should be focused. However the fact that such fundamental work is likely to be carried out next year by the AWWARF and that the costs of the membrane process are so high, indicates that further work with colour removal using membranes should not be considered a priority. Nevertheless, keeping up to date with progress of the membrane work should be actively pursued particularly in view of the superior quality of the membrane product water.

It is therefore proposed that the continued investigations with ozonation followed by biologically enhanced filtration consist of a larger scale pilot plant investigation at a Cape waterworks. The plant would be operated continuously for a period of six to eight months during which specific data including BDOC would be captured to assess the state of the biomass in filter, the influence of nutrients in the feed water and the effect of empty bed contact time and backwashing on the performance of the system. It is proposed that the filter media used be both sand and GAC as in the Duivenhoks pilot study. It has recently been established that a special type of GAC is now being produced, designed specifically to enhance biological activity upon its surface. If possible such GAC would be used in the one filter. As far as chemical analyses are concerned techniques would be required for determining the biodegradability of the feed water to and from the ozonation/filter combination as well as for determining the final disinfection requirements of the water.

The overall objective of the study would be to attempt to optimise the ozonation/filtration process for colour removal such that an assessment could be made of the overall treatment train, to enable design parameters to be established.

Following the proposed investigations it should be possible to make recommendations regarding the use of this process at existing waterworks, and suitable design parameters should have been obtained to enable at least preliminary design of full scale systems to be made.

It is expected that this would be a two year project with a budget cost of approximately R0,6 million (excluding VAT) assuming that the waterworks could provide operating personnel.

8. RECOMMENDATIONS

It is recommended that this report be accepted as the final report for the current WRC funded project on the use of membrane separation and ozonation for the removal of natural colour from Cape waters. It is also recommended that serious consideration be given to the proposal for further investigations with the use of ozonation followed by biologically enhanced filtration for colour removal to arrive at design parameters for full scale installations.

9. ACKNOWLEDGEMENTS

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10.

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ANNEXURE A
REPORT BY HA DE VILLIERS
ON SEMI-TECH BENCH
SCALE MEMBRANE TESTS

CONFIDENTIAL

COLOUR REMOVAL FROM CAPE WATERS
REPORT ON SELECTION AND
LABORATORY EVALUATION OF MEMBRANES

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Report submitted to:
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Stellenbosch
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File Number: 6/445/3
Report Number: 6/92

INITIAL SELECTION TESTS

The initial selection tests were performed on a water sample collected from the Duiwenhoks River on 28 January 1992 - ten 25 L containers being dispatched to Eufrotech, Johannesburg by courier service, while two 200 L drums (plastic) were stored at Membratex, Paarl. The water sent to Eufrotech was used to evaluate the performance of nanofiltration membranes manufactured by Osmonics, while locally manufactured ultrafiltration and cellulose acetate nanofiltration membranes were tested at Membratex.

Six membranes were tested in the standard membrane test rig at Membratex, each with an effective length of 1.0 m and area of 0.0399 m². The membranes were connected in series, with all the water (reject and permeate) being recycled back to the feed container once the required concentration had been reached.

The UF membranes tested were standard Membratex PES 719 and 442 types, with the following characteristics:

442 UF Membrane: Tested on 6000 mol mass Polyethylene Glycol (PEG).

200 kPa	Flux: 56 L/m ² .h	Rejection: 98.4 %
500 kPa	Flux: 87 L/m ² .h	Rejection: 89.9 %

719 UF Membrane: Tested on 40000 mol mass PEG.

500 kPa	Flux: 50 L/m ² .h	Rejection: 95.0 %
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The cellulose acetate membranes tested were manufactured by the Institute for Polymer Science, University of Stellenbosch, and were designated:

BCA 70 :

BCA 75 : Specifications not supplied, but listed in order

BCA 80 : of increasing rejection or density.

(Note: The BCA designation refers only to the formulation run number)

The feed water for all the tests had the following characteristics:

	Unfiltered	Filtered (0.45 µm)
Colour (Hazen or Pt mg/L)	300	450
Absorbance at 545 nm	0.743	0.223
Absorbance at 275 nm	4.357	4.357
Absorbance at 254 nm	4.302	4.302

Tests on the Ultrafiltration membranes

Two test runs were performed, one at 400 kPa and the next at 700 kPa. In each case a stabilization period of 30 minutes was allowed before commencing readings. Two membranes of each type were used, the average flux (corrected to 25 °C) being reported, while the colour and absorbance tests were done on a composite sample in each case. The results are shown in Table 1.

The flux results obtained are somewhat strange, the 442 membrane which has the higher rejection giving a higher flux than the more open 719 membrane as the pressure is increased. This could be attributed to more rapid fouling occurring in the more open pores of the latter membrane, with consequent rapid loss of flux.

In terms of colour rejection, both membranes are marginal at start-up and progressively improve as the fouling layer builds up, reaching quite respectable values after 30 minutes of operation. Unfortunately the flux loss is also very rapid and it is doubtful if these membranes would be suitable for full scale application for colour removal. It all depends on how easily they can be cleaned, the frequency of cleaning and the actual acceptable degree of colour that can be tolerated in the final product.

Tests on Cellulose Acetate membranes

Three test runs were performed on the cellulose acetate membranes, at 400, 700 and 1000 kPa. A stabilization period of at least 30 minutes was allowed after each pressure change before testing. Two membranes of each type were used, the average flux values, corrected to 25 °C, being reported, while the colour and absorbance results shown were done on composite samples.

The results show that all three membrane types give satisfactory results in terms of colour rejection, discounting the high value obtained at 700 kPa on the BCA 75 membrane due to a seal failure on one tube. The flux results are again somewhat variable, but the denser BCA 80 appears to perform the best overall especially at the higher pressures.

It must be noted that these membranes were experimental models developed by IPS and according to the developers the performance of later versions should be considerably better. However, it was also pointed out that the flux values found during the relatively brief test would be about 25 % higher than would be achieved on average when operating continuously on a full scale plant. They felt that a sufficiently long stabilization period had not been allowed for compaction and other effects.

It is not clear whether the characteristics of these membranes are in any way similar to those of the CA spiral wrap units that may be used for the pilot study.

CONTINUOUS OPERATION AND FOULING/CLEANING TESTS

Water used for test

Six cubic metres of water was fetched from the Duiwenhoks river on 12 May 1992 and delivered to Membratex on 13 May where it was pumped into three holding tanks. The full analysis of a sample of this water is given in Table 3. As the colour was considerably lower than expected, the plant operator was contacted to find the reason. According to him it was due to heavy rain in the area prior to collection of the test batch.

Membranes used for test

Ultrafiltration Membranes

Two standard Membratex tubular types were used, in a six tube test rig normally used for quality evaluation purposes. Three type 719 and three type 442 membranes were fitted to this rig to operate in series from the low pressure pump. The characteristics of these membranes have been described under "Initial Selection Tests".

A standard 50 mm capillary UF membrane manufactured by IPS supplied by Membratex was also evaluated. This unit was coupled in series with the tubular UF test rig, after the tubular units, as shown in Figure 1. The available specifications for this unit are:

Effective membrane area	0.301 m ²
Feed inlet area	1.86 x 10 ⁻⁴ m ²
Mol mass cut-off	35000 - 37000 (Tested on PEG)
No pressure specifications given	

Cellulose Acetate Membranes

Six tubular cellulose acetate membranes, manufactured by IPS, were tested in a six tube test rig normally used for quality evaluation purposes. These membranes were essentially the same as the higher rejection membranes used in the initial evaluation, but were from a different batch. The feed water was first passed through the spiral wrap module before entering the six in series CA tubes, as shown in Figure 1.

Spiral Wrap Nanofiltration Membrane

A 2.5" diameter DESAL-5 Thin Film Nanofiltration Membrane Model 2540 was used for this evaluation. The specifications are as follows:

180 molecular mass cut-off	
Typical operating range	5 to 28 bar (500 to 2800 kPa)
Maximum pressure	41 bar (4100 kPa)
Maximum temperature	50 °C
Cleaning pH range	2 to 11.5
Chlorine tolerance	2000 ppm-hours (Dechlorination recommended)
Membrane performance	

98 % rejection on 2 % Fructose (180 mol mass) at 100 psig

15 % rejection on 1000 ppm NaCl (58.5 mm) at 100 psig

96 % rejection on 1000 ppm MgSO₄ (120 mm) at 100 psig

Flux performance not available for the 2.5" element, but for the 4" diam 40" long element it is given as 2800 US gpd. No indication of the actual membrane area is supplied by the manufacturers, so it was not possible to calculate actual fluxes during the test. In the test results "Flux L/h" is the actual total output of the element.

TEST RIG CONFIGURATION

The test rig is shown in Figure 1. The water was fed from the 2200 L feed tank via a float valve to the two concentrate tanks which were interconnected. Each of these acted as an intermediate feed tank to either the high or low pressure circuit, with any loss being replaced from the feed tank.

The low pressure circuit comprised a Mono feed pump (Max pressure 400 kPa) feeding the six UF tubular membranes in series, with the concentrate (reject) being passed into the capillary module. The reject from this unit was returned to the intermediate feed tank. Under normal operating conditions the permeate from this system was run to waste, but could be returned to the intermediate feed tank when required.

The high pressure circuit comprised a Lowara centrifugal booster pump, a cartridge filter, a Hydracell positive displacement pump and a pressure regulator feeding the spiral wrap module. The concentrate (reject) from the SW was fed to the six tubular CA membranes in series, the reject from these being returned to the intermediate feed tank. Part of the SW reject was also returned directly to the tank. Normally all the permeate from the spiral unit was returned to the same Intermediate feed tank.

The linear flow velocity in the tubular CA and UF systems was generally maintained at 1.5 m/s.

The temperature of the feed/concentrate was regulated, to prevent excessive heat build up, by circulating tap water through coils in the intermediate feed tanks.

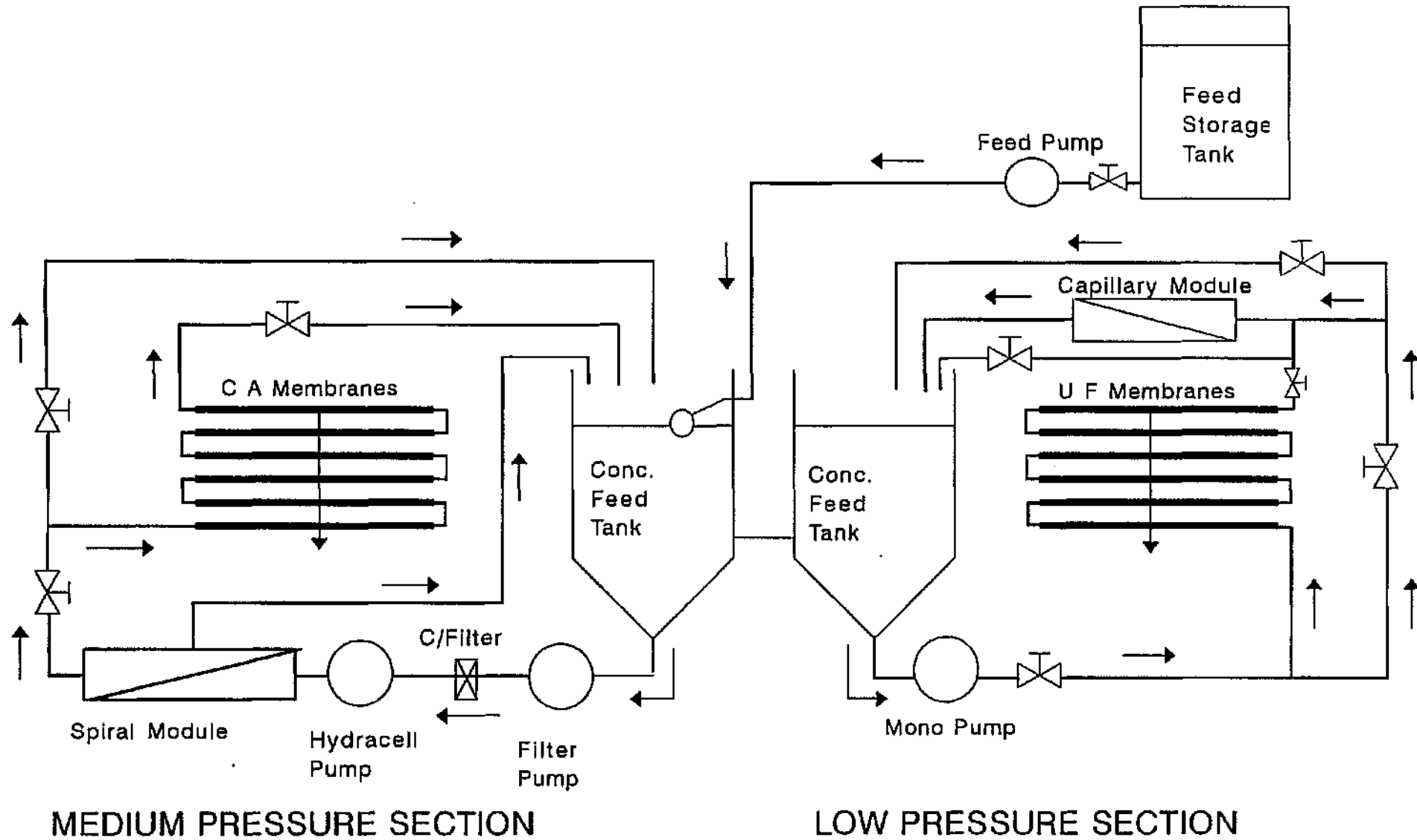


FIGURE 1: MEMBRANE TEST RIG

The overall system could be operated in a concentration or a feed and bleed mode, depending on the requirements.

OPERATION AND RESULTS

The test was run for a total of 25 days, from 9 June till 25 July 1992. The overall operation results as presented by the Membratex staff who were responsible for the day to day operation of the test rig are shown in Table 4 while the results for the individual membranes/modules are presented in Tables 5 to 9. Table 10 summarizes the analytical results, giving the main colour parameters, i.e. Absorbance at 455 nm and Hazen units (or Pt mg/L) done on a Lovibond comparator.

From 9 June till 15 June all the concentrate was returned to the feed tanks to attempt to simulate operation at 90 % recovery, while part of the permeate produced was dumped. The volume of permeate removed is reflected in Table 4 in the third column (Volume). From 16 June the system was operated in a feed and bleed (F&B) mode, the figures given in the third column reflecting the volume of concentrate plus permeate dumped and replaced by an equal volume of feed water via the float valve inlet. The total volumes over the elapsed period are shown. Generally it proved to be almost impossible to maintain any fixed concentration in the feed tank as there were too many variables involved and no means available, other than calculation, of determining the degree of concentration or theoretical recovery. Neither colour or any of the dissolved salt species could be used to give an indication of the concentration, as the colouring material tended to flocculate and lodge on the membranes or in the tanks, while the salts were rejected in variable amounts by the different membranes.

719 AND 442 UF Membrane Performance

The two tubular UF membranes were operated in series from 9 June till 29 June 1992. Results are shown in Tables 5 and 6. The initial fluxes on both were high, being 105 and 110 $\text{L.m}^{-2}.\text{h}^{-1}$ for the 719 and 442 respectively. Overnight (16 hours) the flux had dropped to approximately 35 $\text{L.m}^{-2}.\text{h}^{-1}$ and then continued to decline gradually to 10 to 12 $\text{L.m}^{-2}.\text{h}^{-1}$ where it appeared to stabilize. Passing sponge balls through the system (19/6 to 22/6) gave negligible improvement. An extensive chemical washing with NaOH, Sodium Hypochlorite, Dygest 1 and 2 (commercial neutral cleaning preparations used in industry), 0.5 % EDTA, H_2SO_4 , all provided a cleaning action, but it was reported that the 0.5 % EDTA gave the best results. In all, it was possible to restore the flux to 72 to 75 $\text{L.m}^{-2}.\text{h}^{-1}$ in the 719 and 442 membranes.

The colour removal capability of both membranes was poor (Refer to Table 10). Although both could remove 80 to 90 % of the feed water colour, the remaining amount was not acceptable, the permeate having a residual colour of 10 to 90 mg/L Pt.

Capillary Module Performance

The capillary module which was operated in series with the two UF membranes, had a rated clean water flux of $135 \text{ L.m}^{-2}.\text{h}^{-1}$ at 200 kPa. But almost immediately after start-up on 9 June the flux had deteriorated to $40 \text{ L.m}^{-2}.\text{h}^{-1}$. The flux gradually continued decreasing and reached $21 \text{ L.m}^{-2}.\text{h}^{-1}$ by 22 June. The module was then subjected to the same cleaning procedures as the UF membranes, without the sponge ball cleaning of course, which improved the flux to $41 \text{ L.m}^{-2}.\text{h}^{-1}$ after restarting on 25 June. Further cleaning on 30 June improved the flux marginally. Cleaning with NaOH at Ph 12 for 20 minutes on 2 July effected a considerable improvement, the flux increasing to over $50 \text{ L.m}^{-2}.\text{h}^{-1}$.

The colour removal was initially poor, even when the membrane had extensively fouled, by 15 June (see Table 10). The Hazen colour of the permeate was between 70 and 150 mg/L Pt during this initial period, strangely deteriorating as the flux decreased. After cleaning the module on 22 to 25 June, the colour removal improved considerably, the colour of the permeate varying between 10 and 20 mg/L Pt.

CA Tubular Membranes Performance

The CA tubular membranes were operated in series with the spiral wrap unit, being fed off its reject stream. The clean water flux on these membranes was supposed to be in excess of $75 \text{ L.m}^{-2}.\text{h}^{-1}$. A flux of $52 \text{ L.m}^{-2}.\text{h}^{-1}$ was measured 16 hours after start-up but this dropped steadily to about $12 \text{ L.m}^{-2}.\text{h}^{-1}$ on average before cleaning with DYGEST solution on 24 June. The flux subsequently increased considerably to as high as $77 \text{ L.m}^{-2}.\text{h}^{-1}$ shortly after cleaning, but by 1 July it had again dropped to $22 \text{ L.m}^{-2}.\text{h}^{-1}$. A further cleaning with a 1 % sodium hexametaphosphate solution for one hour again improved the flux to $47 \text{ L.m}^{-2}.\text{h}^{-1}$.

Under all conditions the CA membrane exhibited a very good degree of colour rejection. The lowest reported values are generally <5 or $<10 \text{ mg/L Pt}$, which was attained under all conditions. In terms of the absorbance measurement at 455 nm the CA membranes performed only fractionally worse than the spiral wrap unit, but for most applications, especially for normal domestic purposes, the degree of colour removal was adequate.

A fair degree of salt rejection was also achieved, and on average a rejection (on TDS) of 40 to 50 % may be attained in practice.

Spiral Wrap Nanofiltration Module Performance

The SW module initially produced an output of 173 L/h after being in operation for 16 hours on 10 June. The output dropped rapidly until 23 June when it reached 30 L/h, before it was cleaned with a NaOH solution (at pH 11.4). This improved the output to 70 L/h, from where it gradually deteriorated to 37 L/h on 1 July.

The fouled membrane was then standardized on a 1000 mg/L MgSO_4 feed solution at a pressure of 700 kPa, and at 10 % recovery. Two CIP operations followed, the first being on a 1 % sodium hexametaphosphate solution for 60 minutes, the second being on a NaOH solution at pH 11 for 15 minutes.

Before cleaning the flux was found to be 28.6 L/h at 19.5 °C with a 91.6 % rejection. After cleaning the flux increased to 107.8 L/h at 17 °C, but the rejection decreased to 83.6 %.

When put into operation on the test water after the cleaning and standardization operations, the output had increased to over 150 L/h, and had increased to 167 L/h when the test was stopped on 3 July.

The performance in terms of colour removal was excellent. The Hazen colour was always below the lower reported limit. In terms of absorbance at 455 nm it was also exceptionally good, performing the best of the membranes tested. The salt rejection, based on conductivity, was greater than 60 % in most cases, even after cleaning. The removal of THM precursors was also high, as shown in Table 9.

CONCLUSIONS AND RECOMMENDATIONS

The tests have demonstrated that the colouring material present in the Duiwenhoks water rapidly fouls all the membranes tested, but in most cases the fouling layer can be removed by chemical cleaning.

The nanofiltration spiral wrap and the cellulose acetate membranes gave a very satisfactory degree of colour removal, while the more "open" UF membranes generally failed in this respect. The possibly higher flux of the latter membranes was counteracted by the more rapid fouling that occurred, which would in practice necessitate very frequent cleaning.

The spiral wrap module was very successfully cleaned using a 1 % sodium hexametaphosphate solution followed by a sodium hydroxide solution (pH 11). Sponge ball cleaning of the tubular membranes had little effect on the flux, and generally chemical cleaning would be necessary. The CA membranes showed good flux recovery when cleaned with DYGEST solution, but a 1 % sodium hexametaphosphate solution was less successful.

Although this test was not performed with frequent well spaced cleaning intervals as originally planned, it did indicate that the membranes of choice for further evaluation on a pilot scale must be the DESAL spiral wrap and a cellulose acetate membrane, either in spiral or tubular configuration. The average flux will be relatively conservative, as fouling occurs rapidly, but fortunately it appears to be easily removed by correct, relatively inexpensive, chemical cleaning procedures. A disadvantage would be the down time for cleaning, but this will have to be accommodated by designing in some excess capacity.

TABLE 1

RESULTS OF ULTRAFILTRATION MEMBRANE SELECTION TESTS

Membrane Type	Pressure kPa	Temp °C	Avg. Flux LMH	Colour Pt mg/L	Absorbance 545 nm	Absorbance 275 nm	Absorbance 254 nm
719	400	22.5	143.4	10	0.008	0.451	0.581
442	400	22.5	93.6	5	0.007	0.288	0.376
719	700	23.2	123.3	5	0.005	0.195	0.255
442	700	23.2	159.6	5	0.007	0.363	0.470

TABLE 2

RESULTS OF CELLULOSE ACETATE MEMBRANE TESTS

Membrane Type	Pressure kPa	Temp °C	Avg. Flux LMH	Colour Pt mg/L	Absorbance 545 nm	Absorbance 275 nm	Absorbance 254 nm
BCA 70	400	22.5	22.8	<5	0.006	0.110	0.128
BCA 75	400	22.5	24.5	<5	0.003	0.064	0.108
BCA 80	400	22.5	24.1	<5	0.004	0.073	0.095
BCA 70	700	23.8	50.2	<5	0.006	0.100	0.117
BCA 75	700	23.2	58.7	15	0.037	0.438	0.527
BCA 80	700	23.2	56.8	<5	0.003	0.073	0.095
BCA 70	1000	23.5	81.5	<5	0.005	0.092	0.109
BCA 75	1000	23.5	74.5	<5	0.003	0.082	0.098
BCA 80	1000	23.5	89.6	<5	0.006	0.121	0.144

TABLE 3

**ANALYSIS OF WATER FROM DUIWENHOKS
USED FOR MEMBRANE STUDY**

BATCH COLLECTED ON 12 MAY 1992

Potassium as K mg/L	1.3
Sodium as Na mg/L	25
Calcium as Ca mg/L	2.2
Magnesium as Mg mg/L	3.9
Sulphate as SO ₄ mg/L	13
Chloride as Cl mg/L	40
Alkalinity as CaCO ₃ mg/L	9
ABS 545 nm	0.122
ABS 400 nm	0.473
ABS 275 nm	2.902
ABS 254 nm	3.528
Dissolved Organic Carbon as C mg/L	12.5
Total Organic Carbon as C mg/L	15
Colour as Pt mg/L	200
Turbidity Ntu	35
Suspended solids mg/L	RNO
Conductivity mS/m	18.5
pH (Field)	-
pH (Lab)	6.6
Saturation pH (pHs 20 ½C)	10.3
Total Dissolved Solids (Calc) mg/L	118
Total Hardness as CaCO ₃ mg/L	22
% Balance	1.79
CATIONS meq/L	1.55
ANIONS meq/L	1.58

TABLE 4

BENCH STUDY AT MEMBRATEK, PAARL - 9 JUNE 1992 TO 3 JULY 1992

			ULTRAFILTRATION MEMBRANES					CAPILLARY MODULE			CA MEMBRANES				SPIRAL WRAP MODULE			CALCULATED VALUES								
Date	Time	Volume	Pin	Ream	Temp	Flux719	Flux142	Pin	Post	Fluxcap	Pin	Post	Temp	Fluxco	Pin	Post	Fluxspir	Recovery	Hours	Flux719 (LMH)	Flux142 (LMH)	Fluxcapd (LMH)	Fluxca (LMH)	Fluxspir (LMH)		
9/6	16:00		390	650	11.0	29.1	27.6	200	40	30.2								0.000	0.0	105.011	110.726	39.603				
10/6	08:00		390	650	26.3	23.4	26.2	200	33	27.3	1050	870	14.0	29.1	1100	1030	10.4	0.000	16.0	51.783	34.649	43.493	32.302	173.077		
	11:00	220	380	630	26.2	27.7	21.3	200	30	31.2	1150	890	27.0	34.2	1200	1200	10.2	0.564	19.0	34.069	33.397	38.534	44.677	176.471		
	14:00	200	370	630	26.7	21.7	21.0	200	30	28.8	1150	890	26.7	37.9	1200	1150	13.6	0.689	22.0	33.326	33.127	41.528	40.317	132.313		
	16:00	155	380	630	26.3	100.3	100.7	200	32	31.6	1200	880	26.3	32.4	1300	1200	15.4	0.710	24.0	30.469	30.348	37.549	29.161	116.683		
11/6	08:00		385	630	26.2	134.4	138.0	200	34	32.0	1000	890	26.3	39.7	1050	1000	20.9	0.710	40.0	22.738	22.143	37.313	25.593	86.124		
	11:30	200	385	630	27.4	144.3	130.0	200	31	33.6	1050	915	23.0	63.0	1100	1050	22.9	0.103	45.0	21.149	20.274	33.596	23.506	71.605		
	13:30	200	385	630	26.4	135.6	137.7	200	32	37.8	1050	915	24.0	64.4	1100	1050	24.9	0.137	48.0	19.640	19.379	31.641	25.727	72.249		
12/6	08:03		390	630	25.0	171.7	174.1	200	37	39.3	1150	1000	24.0	74.0	1400	1150	29.1	0.137	64.0	17.799	17.333	30.279	20.649	61.156		
	11:45	180	395	640	24.0	166.7	183.2	200	32	40.0	1000	870	24.0	60.7	1100	1000	32.9	0.146	67.0	16.193	16.681	29.900	18.974	54.711		
	16:00	160																0.131	72.0							
13/6	08:06	220	385	640	20.3	218.0	227.0	210	40	50.0	1050	920	20.3	130.0	1150	1050	45.0	0.900	51.0	11.843	10.648	23.910	11.754	40.000		
	14:13		390	630	24.2	241.0	243.0	200	33	49.0	1100	935	24.0	95.0	1200	1100	42.0	0.900	94.0	12.681	12.574	24.408	16.450	42.157		
16/6	13:00	FAB (320)	400	630	19.2	294.0	260.0	210	40	31.3	1100	950	18.9	146.0	1200	1100	50.7	0.900	116.0	10.395	11.754	23.089	10.464	33.509		
17/6	14:30		400	630	20.0	318.0	270.0	205	40	48.1	1000	870	20.0	112.0	1100	1000	51.4	0.900	140.0	9.317	11.319	24.845	8.396	33.019		
18/6	11:30		410	630	19.3	263.0	240.0	215	40	34.3	1000	910	19.3	124.0	1100	1000	53.2	0.900	162.0	11.620	10.914	22.026	12.323	34.483		
19/6	16:00		400	610	20.2	213.0	300.0	215	38	32.3	1100	925	19.8	170.0	1200	1100	49.5		190.0	11.111	10.187	21.434	8.988	36.364		
22/6	11:05	FAB (400)	380	640	19.4	270.0	244.0	200	39	35.0	1150	950	19.0	61.1	1250	1150	53.3		237.0	11.319	12.523	21.746	23.108	34.413		
23/6	10:13										1100	950	18.3	103.0	950	870	61.3		283.0				14.153	29.364		
23/6	13:00												17.3		1350	1250	23.6		286.0					70.313		
23/6	13:30												17.3		1200	1100	29.3		286.3					61.433		
24/6	12:00										1050	890	17.3	24.1					306.3				63.403			
24/6	16:30										1160	900	19.0	19.7	1200	1100	34.3		310.3				77.364	52.478		
25/6	11:00				19.0			200	33	28.7									330.3				41.673			
25/6	13:30		380	720	19.3	41.3	40.3	195	30	28.9	1100	950	19.3	20.3	1200	1100	35.3		334.0	72.347	73.457	41.383	74.337	50.704		
26/6	14:30	FAB (400)	390	700	19.2	37.4	34.3	195	30	28.5	1100	950	19.0	26.0	1300	1200	37.4		333.0	53.036	54.085	41.963	51.770	48.128		
29/6	08:00		400	690	17.6	84.9	73.6	190	32	29.9	1000	890	17.3	33.8	1100	1000	42.0		417.0	33.996	40.424	40.000	43.206	42.557		
30/6	08:43										950	890	26.3	29.6	1050	950	34.7		441.0				51.633	51.173		
30/6	17:00				20.7			200	41	23.0	1050	990	20.3	40.3	1150	1050	34.5		449.0			47.841	38.010	52.174		
1/7	08:00	FAB (400)			18.3			200	44	27.0	1050	950	18.3	70.0	1200	1050	48.4		464.0			44.277	21.629	37.190		
2/7	13:40				14.3			210	42	21.5	1000	940	14.3	33.1	1050	950	11.7		492.0			43.491	21.721	133.146		
2/7	13:30											950	16.7	32.7					494.0				44.728			
3/7	10:00	FAB (700)			15.0			200	35	22.8	1000	930	14.8	36.3	1100	1000	10.9		513.0			32.457	41.863	165.136		
3/7	17:00				17.0			200	30	23.3	1000	915	16.3	45.0	1100	1000	10.8		532.0			30.894	33.956	166.667		
All the data shown above were provided by Membratic Paar)																										

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719 UF MEMBRANE TEST RESULTS

[illegible]

TABLE 7																	
CAPILLARY MODULE TEST RESULTS																	
Date	Time	Run h	P In kPa	P Out kPa	Temp °C	Flux LMH	Recovery %	ABS 545 nm	ABS 455 nm	ABS 275 nm	ABS 254 nm	Colour Pt mg/L	Conduct mS/m	TDS Calc mg/L	Feed Cond mS/m	Reject. % on Cond.	NOTES
06/09	16:00	0	200	40	15.0	39.603	0										
06/10	08:00	16	200	15	26.5	43.491	0										
06/10	11:00	19	200	30	26.2	38.334	56										
06/10	14:00	22	200	30	26.7	41.528	69	0.025	0.064	1.445	1.826	70	38.5	246	45.5	15.4	
06/10	16:00	24	200	32	26.5	37.849	71										
06/11	08:00	40	200	34	26.2	37.375	75	0.042	0.131	2.317	2.900	110	48.5	310	56	13.4	
06/11	11:30	43	200	31	27.4	33.596	80										
06/11	15:30	48	200	32	26.4	31.641	84										
06/12	08:03	64	200	37	25.0	30.279	84	0.049	0.154	2.748	3.421	130	48	307	56	14.3	
06/12	11:45	67	200	32	24.0	29.900	85										
06/12	16:00	72															
06/15	08:00	88	210	40	20.5	23.920	90	0.054	0.178	3.235	3.960	150	54	346	60	10.0	
06/15	14:15	94	200	31	24.2	24.408	90										
06/16	12:00	116	210	40	19.2	23.089	90										
06/17	14:30	140	205	40	20.0	24.865	90										
06/18	11:30	162	215	40	19.5	22.026	90										
06/19	16:00	190	215	38	20.2	21.434	90										
06/22	11:00	257	200	39	19.4	21.746	90										
06/23	10:15	281															
06/23	15:00	286															
06/23	15:30	286.5															
06/24	12:00	306.5															
06/24	16:30	310.5															
06/25	11:00	330.5	200	33	19.0	41.673	90	0.013	0.037	0.659	0.826	20	21	134	25	16.0	
06/25	11:30																Dye test 1 & 2 3 %
06/25	15:30	334	195	30	19.5	41.385	90	0.011	0.033	0.631	0.790	20	21.5	138	25	14.0	
06/26	14:30	355	195	30	19.2	41.965	90	0.011	0.028	0.496	0.626	15	19.5	125	23.5	17.0	
06/29	08:00	417	190	32	17.6	40.000	90	0.011	0.030	0.487	0.614	15	19.5	125	23	15.2	
06/30	08:45	441															
06/30	17:00	449	200	41	20.7	47.841	90										
07/01	08:00	464	200	44	18.5	44.297	90	0.013	0.034	0.539	0.680	15	21	134	25	16.0	
07/01	13:40	492	230	42	14.5	43.491	90										
07/02	15:30	494						0.010	0.026	0.386	0.486	10	17.5	112	26	32.7	
07/02	18:30	497															NaOH at pH 12 (30 min)
07/03	10:00	513	200	53	15.0	52.471	90	0.012	0.034	0.558	0.702	15	20.5	131	24.5	16.3	
07/03	17:00	532	200	50	17.0	50.894	90	0.012	0.029	0.424	0.535	10	20	120	23	13.0	

Dyecon 1 & 2 3 %

NaOH at pH 12 (20 min)

TABLE 9																			
SPINAL WRAP MODULE TEST RESULTS																			
Date	Time	Run h	P In kPa	P Out kPa	Temp °C	Flux L/h	Recovery %	ABS 345 mm	ABS 455 mm	ABS 775 mm	ABS 154 mm	Calcut PI mg/L	Conduct mS/cm	TDS Calc mg/L	Feed Cond mS/cm	Reject % on Cond.	NOTES		
06/09	16:00	8																	
06/10	08:00	16	1100	1090	16.0	(75.07)	0												
06/10	11:00	19	1200	1200	27.0	(79.47)	34												
06/10		22	1200	1150	26.7	(83.35)	49	0.020	0.001	0.001	0.001	< 1	11.2	91	45.3	45.3			
06/10	16:00	24	1200	1200	26.3	(116.10)	71												
06/11	08:00	40	1000	1000	26.3	14.01	75	0.020	0.000	0.000	0.000	< 10	17	127	54	64.1			
06/11	11:00	43	1100	1050	25.0	78.80	80												
06/11	15:00	46	1100	1050	24.0	72.28	84												
06/12	08:00	64	1100	1150	24.0	61.99	84	0.022	0.002	0.000	0.001	< 10	19.3	125	54	49.2			
06/12	16:00	67	1100	1000	24.0	54.71	85												
06/12	18:00	72																	
06/15	08:00	80	1150	1050	20.2	40.00	81	0.020	0.000	0.004	0.004	< 10	21	134	60	49.0			
06/15	14:15	84	1200	1170	24.0	42.85	82												
06/16	08:00	110	1200	1170	18.9	30.50	80												
06/17	04:30	140	1000	1000	20.9	20.51	82												
06/18	11:30	160	1000	1000	19.3	34.40	82												
06/19	16:00	190	1200	1100	19.4	36.34	82												
06/22	11:00	257	1250	1150	19.0	34.41	82												
06/22	18:15	281	850	870	18.3	29.34	82	0.020	0.000	0.004	0.000	< 5	3	19			Before CIP CIP NaOH at pH 11.4 After CIP		
06/23	15:00																		
06/23	15:00	306	1000	1200	15.3	30.35	80	0.020	0.001	0.000	0.001	< 5	3.3	30					
06/23	15:16	306.3	1200	1100	17.3	61.43													
06/24	12:00	308.3			17.3														
06/24	16:30	310.3	1200	1100	18.8	52.47													
06/25	11:00	310.3																	
06/25	13:30	314	1200	1100	19.2	50.30	81	0.022	0.002	0.011	0.010	< 5	27.3	146	25	1			
06/26	14:30	320	1200	1100	18.0	41.20	82												
06/29	08:00	412	1100	1000	17.2	42.85	82												
06/30	08:15	441	1050	850	26.3	51.50	80												
06/30	15:00	449	1150	1050	20.3	52.17	82												
07/01	08:00	464	1200	1050	19.3	57.10	82	0.022	0.016	0.004	0.000	< 5	18.4	67	20	51.4			
07/01	11:00	467																	
07/01	13:00	471																	
07/01	13:40	492	1200	850	14.3	153.14	82												
07/02	13:00	494			16.7			0.020	0.001	0.015	0.010	< 5	8.9	40	20	61.3			
07/02	15:00	512	1100	1000	14.3	140.13	82	0.020	0.001	0.012	0.010	< 5	8.8	35	21.3	64.3			
07/02	17:00	513	1100	1000	18.3	166.67	82	0.020	0.001	0.007	0.002	< 5	7.7	49	23	64.3			
*** STANDARDIZATION 1/7/92 Feed 1000 ppm MgSO4 10 % Recovery 700 kPa pH 5.3-6.3 Before CIP: Flux (Output) = 28.6 L/h Temp 19.3 °C Rejection 91.6 % After CIP: Flux (Output) = 197.5 L/h Temp 17 °C Rejection 83.6 %																			
TDS DETERMINATIONS																			
DATE		SAMPLE		12 Hours after adding 12 mg/L chlorine				Without chlorine											
				CHLCL3	CHLCL2	CHLCL	CHLCL	CHLCL3	CHLCL2	CHLCL	CHLCL								
04/10	Feed			10	21	6	0	0	0	0	0								
04/10	Recovery			11	11	4	0	0	0	0	0								
07/02	Recovery			22	4	2	0	7	0	0	0								

TABLE 10													
COLOUR REMOVAL - SUMMARY OF ANALYTICAL DATA													
DATE	FEED		719 UF		442 UF		Capillary		CA Tubular		Spiral Wrap		NOTES
	Absorbance at 455nm	Colour Pt mg/L	Absorbance at 455nm	Colour Pt mg/L	Absorbance at 455nm	Colour Pt mg/L	Absorbance at 455nm	Colour Pt mg/L	Absorbance at 455nm	Colour Pt mg/L	Absorbance at 455nm	Colour Pt mg/L	
06/10/92	0.663	380	0.122	90	0.074	70	0.084	70	0.002	< 5	0.001	< 5	
06/11/92	0.731	450	0.113	80	0.061	70	0.131	110	0.006	< 10	0.004	< 10	
06/12/92	0.897	600	0.113	90	0.066	80	0.134	130	0.005	< 10	0.002	< 10	
06/13/92	1.213	800	0.121	80	0.093	80	0.178	150	0.013	< 10	0.002	< 10	
06/19/92			0.016	10	0.013	10							Before S/Ball clean
06/22/92			0.016	20	0.034	30							After S/Ball clean
06/23/92											0.012	< 5	Before NaOH pH 11.5
06/23/92											0.011	< 5	After NaOH pH 11.5
06/25/92	0.332	350	0.040	30	0.037	30	0.033	20	0.003	< 5	0.002	< 5	
06/26/92	0.606	350					0.028	15					
06/29/92	0.429	350					0.030	15					
07/01/92	0.384	350					0.034	15	0.012	10	0.018	< 5	
07/02/92	0.539	350					0.026	19	0.017	< 5	0.001	< 5	
07/03/92	0.503	350					0.034	15	0.006	< 5	0.001	< 5	
07/03/92	0.602	350					0.029	18	0.019	< 5	0.001	< 5	