

PURIFICATION OF WATER BY ULTRAFILTRATION

by

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INTRODUCTION

Ultrapure, deionised, and pyrogen-free waters are important commodities. In many industries, product quality, or process performance are significantly influenced by the quality of the water used. For example, particle-free water is required in the polymer processing and chemical industries. In the polymer processing industry, suspended matter interferes with polymerisation reactions, and in the chemical industry, the purity of product may be affected by the process water quality. Deionised and particle-free water is required by the electronics industry, and pyrogen-free water is required for the food, medical and pharmaceutical industries. The production of purified water is also necessary for closed circuit cooling systems and boiler feed waters, where there is a direct relationship between water quality and operating costs. For example, in the power industry, seasonal variations in colloidal silica content of boiler feed water have a pronounced effect on the blowdown rate required to prevent build-up of scale on heating surfaces (ref. 1).

The conventional approach to the production of ultrapure water is to use distillation, possibly followed by deionisation. For boiler feed the methods include chemical coagulation, mixed-media filtration and ion exchange. However, there is growing interest in the use of membranes to produce directly, or provide pretreatment in the production of, ultrapure and high quality boiler feed water (ref. 2), (ref. 3), (ref. 4), (ref. 5).

Ultrafiltration membranes, which are capable of rejecting macromolecules, should be able to readily retain suspended and colloidal solids, such as micro-organisms, virus, phage, silica and metal oxides. Depending on the usage, downstream treatment by UV, or further membrane treatment (i.e. reverse osmosis), may be necessary to guarantee sterility or lower total dissolved solids. Reverse osmosis alone would not be sufficient for the task since most membranes (and especially cellulose acetate) are reported to suffer from the "growing through" of micro-organisms and scaling or fouling due to colloidal solids which leads to the need for pretreatment of the water. Ultrafiltration is of particular interest in this application because of the possible use of a cascade system to remove large particles and salts. However, many ultrafiltration membranes are themselves sensitive to silica, iron, manganese, and hardness (ref. 6), and there is a clear need for less sensitive membranes.

In this paper we discuss the performance of a newly developed polyamide membrane (ref. 7), (ref. 8) in the production of purified water. The performance of the membrane with respect to silica sensitivity is compared with that of commercially available polysulphone membranes. The novel polyamide membrane has been evaluated in two different types

of hardware; the DDS Lab. Module 35, and a newly developed capillary ultrafiltration cartridge (ref. 9). Comparisons are also made of the energy requirements in the production of ultrafiltered water by the classical high pressure equipment, and the capillary ultrafiltration module at low pressure.

EXPERIMENTAL

For the high pressure work, membranes were fitted to a DDS Module 35, shown schematically in Figure 1. The DDS Module is a flat plate ultrafiltration unit with elliptical plates and a membrane area of 2.25 sq.m. The unit operates with a feed crossflow of about 12 cu.m/hr. or 1.5 m/s, at typical inlet and outlet pressures of 700kPa and 240kPa, with no back pressure on the permeate.

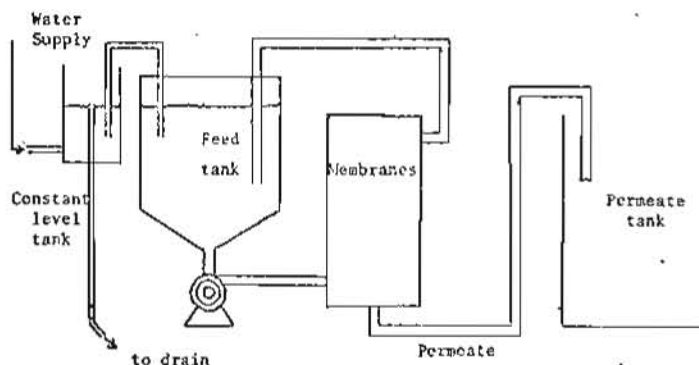


Figure 1. DDS Elliptical Module Equipment Schematic (Experiments 1, 2 and 3).

The low pressure equipment was a capillary ultrafiltration cartridge produced in Australia under patent (ref. 8). The capillary unit comprises a series of flat plates supporting the membranes, and providing a micro-channel of variable channel height which depends upon the pressure. Suitable pressures range from 10 to 30 psi (70 to 200kPa). This concept provides for enhanced shear rate across the surface of the membrane with minimal energy consumption. The capillary modules are used with high porosity membranes (i.e. those with a high free area - ref. 10), and are best operated at the limiting value of non-gel polarised conditions (i.e. close to but not at gel polarisation). Figure 2 shows the set-up.

A set of three experiments were performed on the high pressure DDS Module 35 fitted with CT32.5 N polyamide membranes developed at the University of New South Wales, and having a molecular weight cut-off of about 35,000 Daltons. The first experiment was to concentrate a feed of untreated Sydney tap water fifty times by collecting the permeate and making up the feed volume directly from the tap. The advantages in concentrating the water in such a manner were firstly, that the effect of retained species on the membrane throughput could be studied under the worst possible conditions for the membrane,

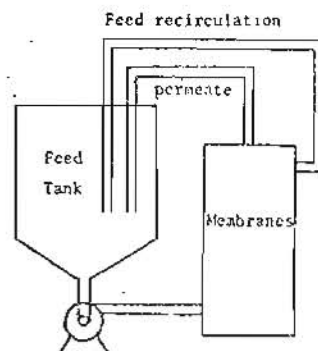


Figure 2. Capillary Module Equipment Schematic (Experiment 4).

and secondly, the higher concentration of solids obtained gave a greater reliability in the analysis of samples. For the second experiment, the tap water was prefiltered through an AMF Cuno water filter with an AP110 cartridge having a 10 micron pore size; in this case, the water was concentrated five times, allowing a shorter period of time for the experiment to be completed. In order to compare the performance of the polyamide membranes with polysulphone membranes, a third experiment was carried out with a pair of DDS GR60P membranes fitted to the module; the GR60P membranes have a nominal molecular weight cut-off of 20,000 Daltons. The CT32.5 N membranes were not replaced for the test. Sydney tap water was concentrated 20 times under similar conditions to the first experiment (i.e. no prefiltration) over a six-hour period.

Using the low pressure capillary cartridge, a fourth experiment on Sydney tap water was carried out using CC27.5 N polyamide membranes, also developed by the University of New South Wales, and with a somewhat higher molecular weight cut-off than the CT32.5 N membranes mentioned above.

For the experiments on the DDS module, a profile was made of the temperature, inlet and outlet pressures, permeate flux, and feed cross-flowrate. Samples of feed, permeate, and concentrate were collected and analysed for solids content, turbidity, and absorbance. The feed volume was kept at a constant 50 litres except for close to the end of the first experiment, when the feed water was turned off to allow a rapid concentration of the feed to take place. Temperatures during the experiments were in the range 25-35 deg. C.

The experiment on the capillary ultrafiltration cartridge was made by recirculating water over a 12 hour period to monitor the flux decline. Initially, the back-pressure was set at 88kPa to compare the pressure required on the cartridge with that required on the DDS module to obtain the same flux. After four hours, the pressure was increased to 100kPa as this is a standard pressure used for comparison purposes, and is the recommended minimum pressure for this application. The cross-flowrate for this experiment was 186 L/hr, and the temperature was approximately 30 deg. C.

It should be noted the DDS Module 35 and the GR60P membranes are strictly intended for classical ultrafiltration applications. In particular the polysulphone membranes are designed for the ultrafiltration of proteinaceous food streams and not specifically for the species present in the water tests. However the DDS system was chosen for comparison on the basis of convenience and its ability to accommodate flat sheet membranes.

RESULTS

Results for the first two experiments are shown in Figures 3 and 4, the data for each being superimposed for comparison. Only minor differences in flux occurred by use of filtered rather than unfiltered water, although the latter had the advantage of being about 5 deg. C warmer. Flux values of about 100 L/sq.m hr were obtained throughout the experiments with a slight rise at the end of the first experiment due to a temperature increase of 10 to 15 dec. C.

Samples of concentrated feed and permeate were analysed for total dry solids content, turbidity, and absorbance, the results of which are shown in Table 1. These analyses provide a rapid means of determining the retentive performance of the membranes. The bar graph in Figure 5 compares the dry solids determinations of Table 1. From these data it can be calculated that there was a 66% rejection of total solids for the feed at the end of the run on unfiltered water, and an 84% rejection of total solids for the prefiltered water in the second experiment. It should be noted however, that the concentration factor in the second experiment was only one tenth that of the first experiment.

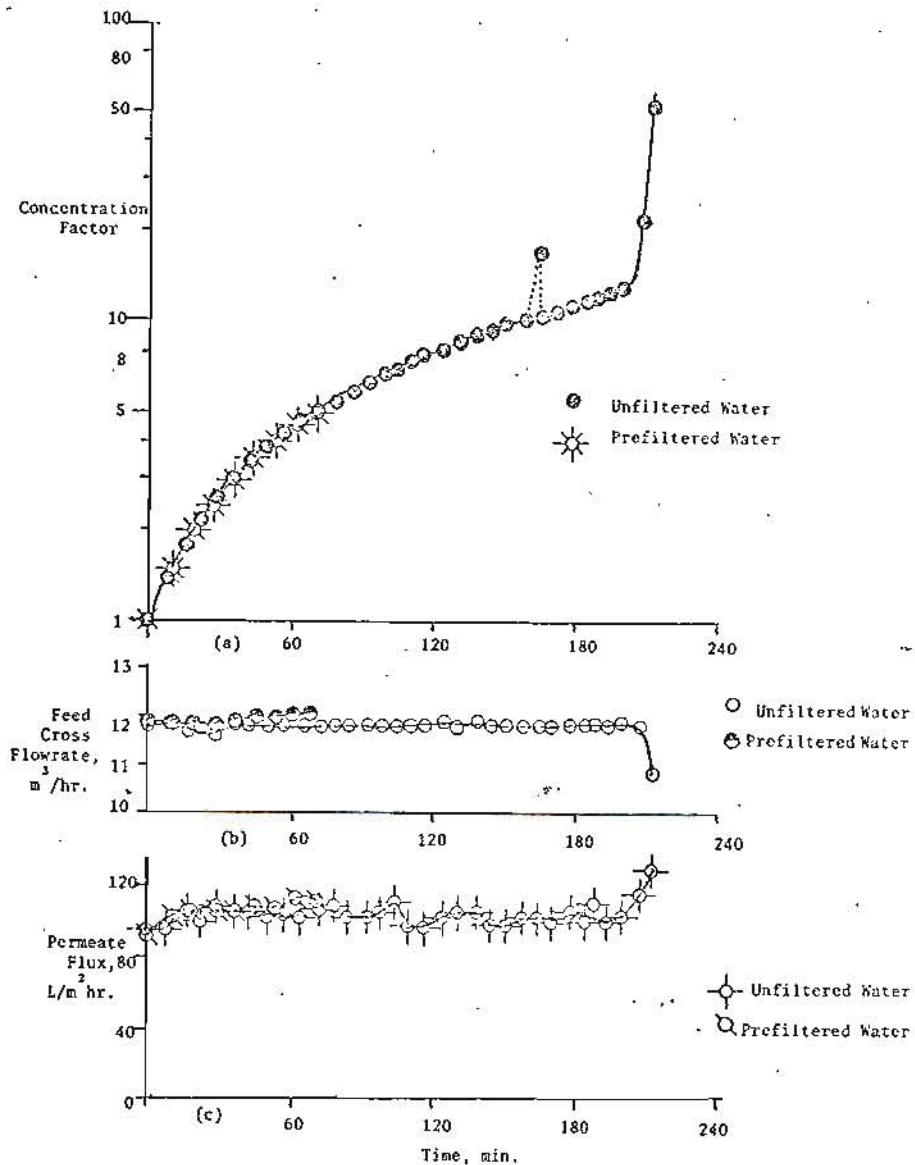


Figure 3. Concentration Factor, Feed Cross Flowrate, and Permeable Flux Profiles for Experiments 1 and 2

One would expect a greater total solids rejection for the first experiment than the second, as in the latter case, most of the larger particles had been filtered out. A possible explanation for this discrepancy is that at the end of the first experiment, the feed cross-flow dropped, and the lower shear rate may have caused a fall in rejection for operation under pre-gel conditions.

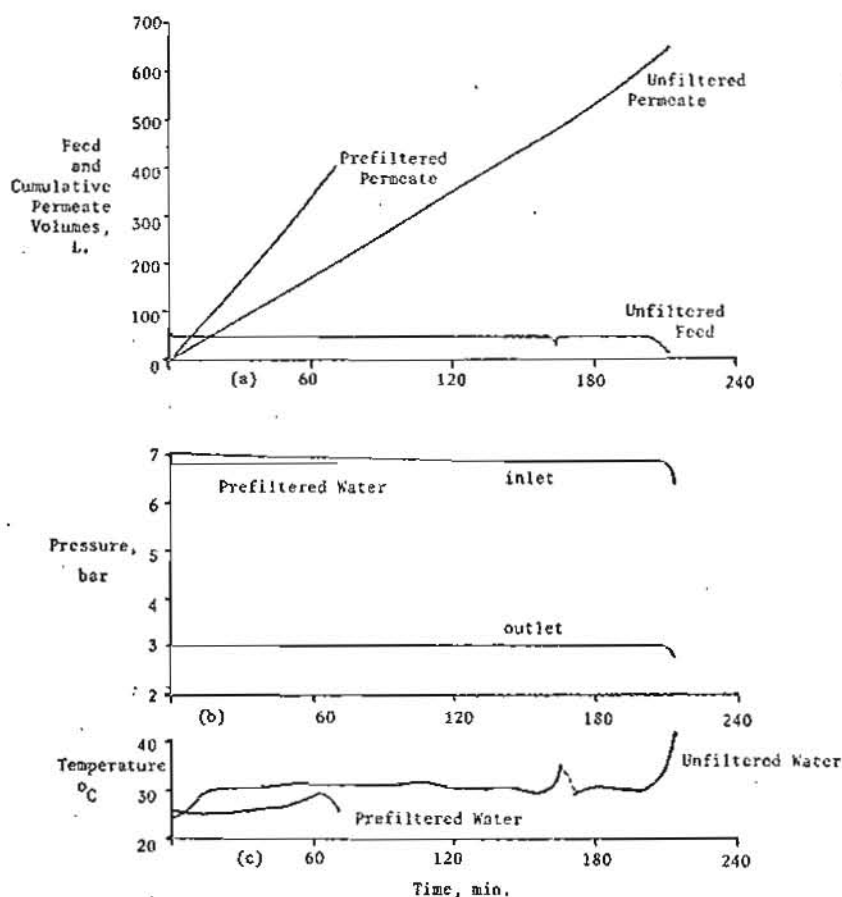


Figure 4. Feed and Permeate Volumes, Pressure, and Temperature Profiles for Experiments 1 and 2.

Figure 6 compares the flux data for the third experiment on the DDS module, with the polyamide membranes and the GR60P polysulphone membranes. The new GR60P membranes showed significantly higher initial flux than the used polyamide membranes. However, the GR60P membranes appeared to be much more sensitive to the retained solids and showed a steady flux decline. On the other hand, the polyamide membrane showed no noticeable sign of flux loss. Extrapolation of the data in Figure 6 suggests that after several hours the polyamide membrane would have a higher flux. Indeed, subsequent long-term tests showed that the polysulphone membrane flux declined to about 75% of the polyamide membrane flux. In terms of rejection the GR60P membrane showed a slight advantage, i.e. 85% versus 66%.

It should be noted that tests carried out in this program were designed to subject the membranes to harsh conditions. Normally, a cleaning cycle would be used to mitigate against flux decline, and in this respect, the polysulphone membrane recovered more than 90% of the initial flux upon cleaning. In practical terms the user may have to choose between an insensitive membrane giving good permeate quality and a sensitive membrane,

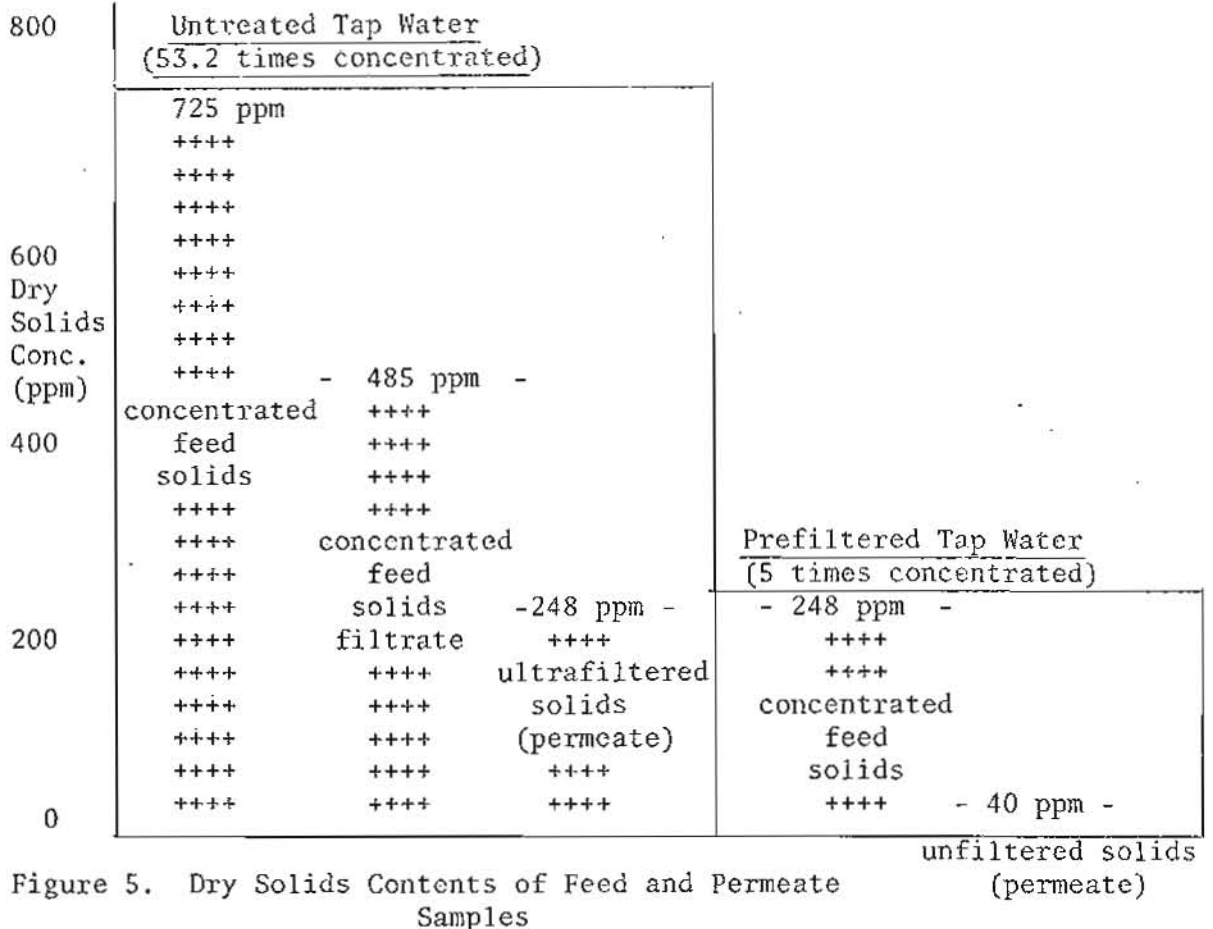


Figure 5. Dry Solids Contents of Feed and Permeate Samples

TABLE 1
Summary of Analyses of Test Samples

Experiment	Sample	Dry solids g/L	Turbidity NTU (1)	Absorbance (2)
1	Feed	0.725	80	0.504
	Filtrate (3)	0.485	-	-
	Permeate	0.248	0.70	0.012
(concentrated 53.2 times)				
2	Feed	0.248	8.3	0.035
	Permeate	0.040	0.30	0.005
(concentrated 5 times)				
3	Feed	0.725	80	0.504
	GR60P Perm	0.108	0.49	0.007
	CT32.5 Perm.	0.248	0.70	0.012
4	Feed	0.19	3.2	0.005
	Permeate	0.08	0.5	0.005
		not concentrated		
Control Samples	DW (4)	-	0.20	0.000
	air	-	0.33	-0.037

- (1) Nephelometric Turbidity Units
- (2) Absorbance Reading @ 450nm (visible range)
- (3) Whatman No. 41 Filter Paper
- (4) Distilled Water

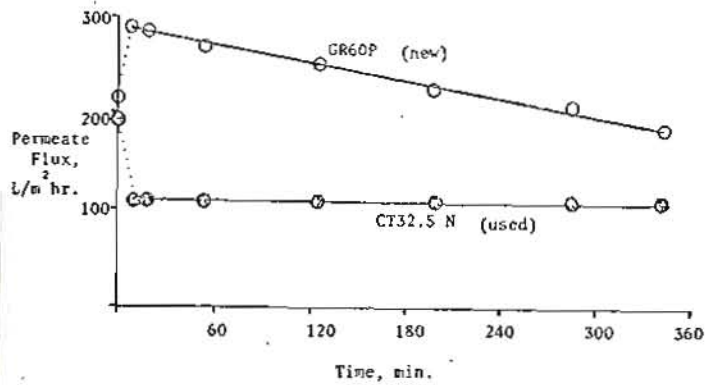


Fig. 6. Comparative Permeate Flux Profiles for Polysulfone (GR60P) and Polyamide (CT32.5N) Membranes on Sydney Tap Water.

requiring frequent cleaning, but giving rather better permeate quality. With respect to ultrapure water production, it has already been established that the polyamide membranes are highly rejecting to micro-organisms (ref.7).

The results of the low pressure experiment on the capillary ultrafiltration cartridge are shown in Figure 7. At an inlet pressure of 88kPa, the stabilised flux was 64 L/sq.m hr. This flux was achieved at a pressure of at least 240kPa in the DDS module, the flux purposely being matched in the cartridge to compare the pressure required for that flux. The pressure drop across the cartridge was 20 kPa. The stabilised flux at 100kPa was 74.3 l/sq.m hr, and showed no decline over the last 8 hours of experiment. Figure 8 shows the flux versus pressure relationship for the cartridge, and indicates that the experiment was carried out in a pre-gel polarised condition. The total dry solids content of 0.19 g/L for the feed and 0.08 g/L for the permeate gave a total solids rejection of 60% for this experiment.

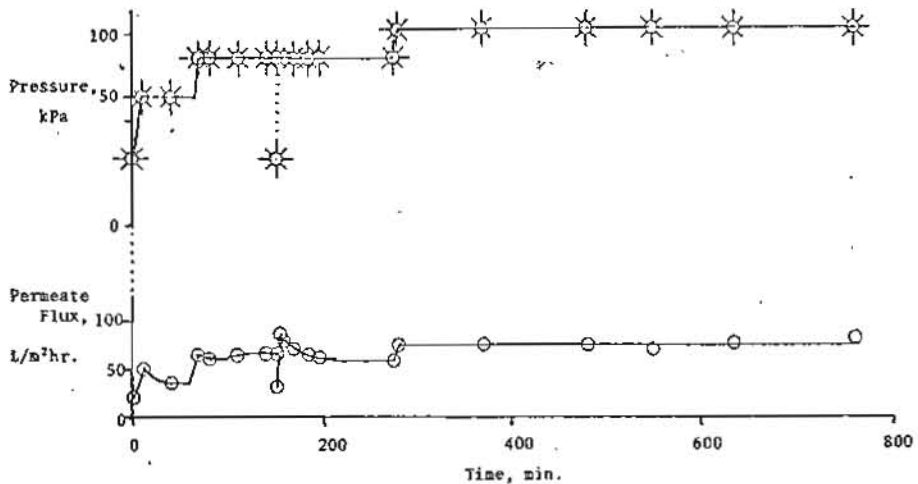


Figure 7. Pressure and Permeate Flux Profiles for Ultrafiltration of Sydney Tap Water on the Capillary Module.

Chemical analyses of a typical permeate from ultrafiltration of Sydney tap water by polyamide membranes indicated that the permeate contained an average of 2.5 ppm silicon, 12.9 ppm calcium, 5.0 ppm magnesium, and no measurable iron, manganese or copper. Hardness for this permeate was also determined at 5.3 mg/L as calcium carbonate equivalent, and the total dissolved solids were 15.2 ug/L. These values are compared in Table 2 with those specified by DDS for process waters (ref. 6).

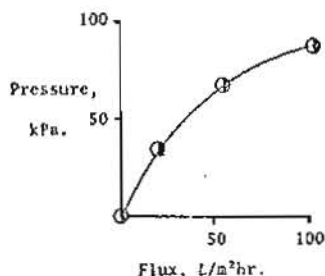


Figure 8. Pressure Versus Flux Relationship for Sydney Tap Water on the Capillary Module.

TABLE 2

Permeate Solids and DDS Specifications for Process Water

	Permeate	DDS Specifications (ref. 6)
Fe	None	0.05 ppm
Mn	None	0.02 ppm
Cu	None	-
Si	2.5 ppm	5.0 ppm
Ca	12.9 ppm	-
Mg	5.0 ppm	-
Hardness (1)	5.3 mg/L	356 mg/L
TDS (2)	0.0152 mg/L	-

(1) Calcium carbonate equivalent

(2) Total Dissolved Solids

In order to evaluate the energy requirements of the elliptical module and capillary cartridge, their pump power was measured under full flow and pressure, and the results are shown in Table 3. Both systems show low energy demand when compared with the 2300MJ/cu.m required for single effect distillation. The cartridge system has an exceptionally low energy demand due to its very small channel height and low operating pressure. These characteristics should lead to lower operating costs, providing membrane replacement and cleaning/sanitation costs can be kept at a minimum.

Another advantage that ultrafiltration has over distillation is that with a membrane system, the bleed taken off the feed can be varied to a greater extent than with distillation when the level of contamination in the water supply varies. For example, if there is a surge of colloidal matter, such as clays, a membrane system can have the bleed turned up from, say, 5% to over 50%. The distillation system, on the other hand, is restricted to smaller adjustments, because of the tight constraints on boiler design.

CONCLUSIONS

Ultrafiltration has been shown to be a viable means of producing purified water for the process industries. The polyamide membranes developed by the University of New South Wales and the DDS GR60P membranes have been shown to be effective barriers to colloidal species. When compared

TABLE 3

Power and Energy Requirements on Membrane Area and
Permeate Volume

	DDS Module		Capillary Cartridge
Pump Type	6 stage centrifugal		gear
Power Supply	3 phase		single phase
Membrane Area (sq. m)	2.25		0.418
Power Consumption (kW)	5.4		0.098
Power per unit Membrane area (kW/sq.m)	2.4		0.21
Feed Crossflow (L/hr.)	12,000		186
Membrane Type	CC27.5 N	GR60 P	CC27.5 N
Membrane Flux (L/sq. m hr)	109	76.3	74.3
Power per Unit Permeate Volume MJ/cu.m.	79.3	113	10.4

with the polysulphone membrane, the polyamide membrane is unaffected in terms of fouling by contaminants in the water, which are probably colloidal silica incorporated in organic detritus as siloxane complexes. Differences between the two types of membrane may be associated with different surface charges for the conditions of the experiments. The fouling components can, however, be removed by cleaning.

Ultrafiltration offers major energy savings in the production of purified water when compared with distillation. Of the two ultrafiltration systems investigated, the capillary cartridge requires almost an order of magnitude less power consumption per unit of purified water, as well as power consumption per unit area of membrane. The final choice of membrane type and housing will depend on a detailed evaluation of required water quality and overall production costs.

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REFERENCES

1. Cecil, L.K., "Complete Water Reuse: Industries' Opportunity", Proc. National Conference on Water Reuse, Washington, DC, (April, 1973).
2. Breslau, B. R. and Testa, A. J., Milnes, B. A., and Medjanis, G., (1980), "Advances in Hollow Fiber Ultrafiltration Technology", in 'Ultrafiltration Membranes and Applications', A. R. Cooper (ed.), Plenum Press, New York, pp. 108-125.
3. Fell, C. J. D., Fane, A. G., Lefebvre, M. S., (1979), "Use of Membrane Barriers to Remove Micro-organisms and Colloidal Species from Solution", Proc. CSIRO Symposium on Filtration and Separation, Ryde, pp. 3/1 - 3/12.
4. Nelsen, L. L., and Reti, A. R., (1980), "Pyrogen Removal by Ultrafiltration", in 'Ultrafiltration Membranes and Applications', A. R. Cooper, (ed.), Plenum Press, New York.
5. Duff, J. H., and Kerr, M. H. (1974), "Boiler Makeup Requirements May Affect Cooling Water Chemistry", vol. 36, Proc. American Power Conference, pp. 753-758.
6. DDS RO-Division, communication to the University of New South Wales via Anderson Equipment, Co-op. Ltd., 22nd November, 1979.
7. Lefebvre, M.S., Fell, C. J. D., Fane, A. G., and Waters, A. G. (1980), "Permeability Parameters of a Novel Polyamide Membrane", in 'Ultrafiltration Membranes and Applications', A. R. Cooper (ed.), Plenum Press, New York, pp. 18-37.
8. Lefebvre, M. S., and Fell, C. J. D., "Anisotropic Multilayered Synthetic Semi-Permeable Membranes", Aust. Patent 505, 494.
9. Lefebvre, M. S., Aust. Prov. Patent PE 5372/80.
10. Fane, A. G., Fell, C. J. D. and Waters, A. G., "The Relationship Between Surface Pore Characteristics and Flux for Ultrafiltration Membranes", J. Memb. Sci., - in press.
11. Breslau, B. R., Agranat, E. A., Testa, A. J., Messinger, S., and Cross, R. A., (1975), "Hollow Fiber Ultrafiltration", Chemical Engineering Progress, 71:12, Dec. '75, pp. 74-80.