# Caustic Management and Reuse in the Beverage Bottling Industry

Report to the

Water Research Commission

by

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# EXECUTIVE SUMMARY

## INTRODUCTION

Sodium hydroxide solution (caustic) is widely used as a cleaning agent in the food and beverage bottling industries. The two main uses are as a cleaning-in-place (CIP) solution and in bottle washers. In CIP applications, a caustic solution with a strength ranging from 5 % to about 20 %, is recirculated through the vessel to be cleaned. During the clean, the caustic solution picks up suspended solids, organics, silicates etc., and hence deteriorates with each clean. The CIP solution is usually used for four to eight cleans before being discarded to drain. In the bottle washing process, the bottles are firstly plunged into a caustic bath ( 2 % to 5 % caustic strength). The caustic bath serves to remove residual labels, glue, grit, residual dehydrated organics etc from the bottles, and hence this bath progressively becomes contaminated with these. When this contamination reaches an unacceptable level, the entire contents of the bath are dumped. Generally, a caustic batch is used for 8 weeks to 10 weeks before being dumped.

In both the CIP and bottle wash bath caustic effluents, the caustic strength of the waste caustic stream is still high, and the stream is discarded solely because of the level of contamination. If the level of contamination is reduced, the effective lifespan of the caustic solution could be extended significantly, implying a significant savings in caustic usage.

Internationally membrane-based systems for the cleanup and reuse of spent caustic solutions are readily available from various commercial vendors. In South Africa, however, cleanup of spent caustic solutions and their subsequent reuse or recycling is rarely practiced. Possible reasons for this include the high cost of imported caustic cleanup systems, the high cost of obtaining spares and new membranes for imported systems, as well as the perception that membranes are a very “high tech” technology that requires very high skills levels to operate and maintain. This is exacerbated by the lack of a local expertise base to support these systems in terms of operations, optimization, modifications etc.

There could be considerable benefit to the South African food and beverage industry and the broader aspect of environmental protection, therefore, if a locally developed caustic cleanup system was available which addressed the above concerns. This forms the overall objective of this project.

## APPROACH

Three membrane systems were chosen for evaluation, based primarily on easy availability locally – a major consideration in determining the cost of systems. These were :- the woven fibre microfilter (WFMF) produced locally by Gelvanor; capillary ultrafilters (CUF) produced locally by FiltRsa; an imported tubular nanofilter (TNF) produced by PCI (England). The latter membrane was selected for evaluation since many overseas caustic cleanup systems use nanofilters, and there are currently no locally produced nanofilters.

| Membrane Type | Supplier and Description | MW Cutoff / Rejection | Size |
|---|---|---|---|
| MF | Gelvanor<br>Woven fibre polyester | N/a | 25 mm diameter, variable length |
| UF | FiltRsa Capillary UF, polysulphone, #1713 | 35 000 | 1.2 mm capillaries, variable length |
| NF | PCI Tubular NF, type AFC30, polyamide film | 75 % $CaCl_2$ | 12.5 mm diameter tubes, length 1.2 m |

The evaluations were based on the following performance criteria :- separation efficiency; permeate fluxes ; resistance to caustic; cleanabilility of the membranes. The separation efficiency was determined from turbidity or suspended solids measurements on the feed and permeate. Resistance to caustic was determined by monitoring whether there was any change in pure water flux and rejection, when the membrane was exposed to caustic. Cleanability of the membranes was determined by assessing whether the fluxes could be easily recovered after many runs.

In initial investigations, waste CIP caustic from the sugar industry was used. This was obtained via the Sugar Milling Research Institute (SMRI) in Durban. However, logistical problems were experienced with obtaining this waste caustic, and the project subsequently focused on cleanup of spent caustic from bottle wash baths in the beverage bottling industry. The waste bottle wash caustic was obtained from ABI Phoenix, also in Durban.

## EVALUATION OF WFMF

WFMF trials were conducted on spent caustic soda samples were obtained from the Sugar Milling Research Institute (SMRI), using both a flat-sheet and crossflow microfiltration rigs. According to SMRI personnel, caustic soda is reused until the viscosity reaches the level where it can no longer be pumped. Typically, the viscosity of fresh caustic is 5.75 cP, whilst the viscosity of waste caustic may be up to 20 cP. The objective is to reduce the viscosity so as to enable extended use of the caustic soda.

Preliminary tests were conducted using a flat sheet test cell. These experiments were conducted in dead-end mode at a pressure of 100 kPa. It was found that the WFMF reduced the viscosity of the spent caustic from 17.2 cP down to 7.1 cP, quite close to that of the fresh caustic. This reduction was regarded as excellent, and indicated that WFMF was capable of cleaning up waste caustic to the point where it could be reused.

Unfortunately however, this excellent result obtained in initial trials could not be repeated in subsequent flat-sheet trials and crossflow trials. Typically, in subsequent evaluations, the WFMF system reduced the spent caustic viscosity from 19.2 cP to 13.2 cP. Whilst it was clear that the WFMF system was effecting some cleanup of the caustic, the reduction in viscosity was insufficient to reuse the caustic.

Various investigations were done to try and improve the performance of the WFMF system. This included changing the operating pressure as well as precoating the membrane. These had no significant effect on system performance. In all instances there was a definite reduction in viscosity, but nothing close to the excellent results obtained initially.

It was concluded that WFMF alone is inadequate to recycle spent CIP solution from the sugar industry. However, WFMF could play a role as a pretreatment step, if it is found that an expensive or exotic membrane is necessary to remove the target contaminants that contribute to the viscosity increase. In this instance, the WFMF could remove the grosser contaminants and thus extend the life of the expensive membrane.

## EVALUATION OF CUF

Preliminary trials on UF were conducted on a flat-sheet rig, using a 35kD cutoff UF membrane obtained from the Institute of Polymer Science, University of Stellenbosch. Two batches of waste caustic obtained from ABI Phoenix were investigated – 3 weeks old and 8 weeks old. The suspended solids content of the feed and permeate were measured as an indication of separation efficiency. The feed suspended solids in the 3 weeks old batch ranged from 100 mg/L to 300 mg/L, while the feed suspended solids in the 8 week old batch was approximately 800 mg/L to 1000 mg/L. The separation efficiency was very good, with the permeate suspended solids ranging from 2 mg/L to 30 mg/L – a reduction of 90 % to 99 %. Interestingly, the permeate suspended solids decreased as the feed suspended solids increased.

This very good separation efficiency was repeatedly obtained in trials on capillary ultrafiltration modules. Here turbidity was used to indicate separation efficiency. Once again, the separation efficiency was a function of the age of the batch. For a 4 weeks old batch the feed turbidity ranged from 300 NTU to 500 NTU, while the permeate turbidity was below 2 NTU. For a 8 week old batch the feed turbidity also ranged from 400 NTU to about 500 NTU. The permeate turbidities ranged from 1 NTU to 10 NTU, with some samples registering 15 NTU. Overall, this indicates that CUF is capable of a very good turbidity removal, and that CUF is capable of cleaning up waste caustic to the point where it could be reused.

Permeate fluxes were measured at an operating pressure of 1 bar and a tube velocity of 1 m/s. Typically, and without any form of flux enhancement, the permeate flux starts off at around 50 LMH and decreases to about 20 LMH after 3 hours of filtration. . Backflushing was investigated as a form of flux enhancement, and proved to be highly effective. Backflushing for 5 minutes after every 1.5 hours of filtration restored the permeate flux to over 90 % of its initial value. This enabled the runtime to be extended substantially. In the longest run performed with backflushing, an average flux of 35 LMH was maintained for 32 hours.

There is a weak dependency on batch age, with permeate fluxes decreasing slightly as the batch age increases With backflushing, an average flux of 42 LMH was obtained for a 3 week batch age, decreasing to 35 LMH for a 6 week batch age.

Three methods of cleaning fouled membranes were investigated – flushing with water, backflushing, and chemical cleaning. Whilst the former two were not very effective in removing the fouling layer, chemical cleaning consistently restored the pure water flux to over 90 % of pure water flux of a new membrane. Chemical cleaning was also able to restore an old fouled membrane that had been out of use for a while. The chemical cleaning solution consisted of EDTA, sodium laurel sulphate and sodium hydroxide in equal parts, made up to a 0.5 m/v solution.

The CUF system also seemed to be very stable when operated on the waste caustic, with no change in separation efficiency, permeate fluxes or pure water fluxes after extended operation.

**EVALUATION OF TNF**

Tubular nanofiltration trials were performed on the ABI caustic at a pressure of 20 bar and a tube velocity of approximately 1 m/s. In between caustic runs, pure water fluxes were determined at different operating pressures.

The permeate turbities range from 0.3 to 3 NTU, for feed turbidities of 250 to 400 NTU, indicating an excellent turbidity rejection. However, these turbidities are higher than would be expected of a nanofilter, where turbidities well below 1 NTU should be achieved.

The average permeate fluxes exhibited a very strange trend. In the first run, a flux of 30 LMH was obtained. In subsequent runs this increased rapidly to 60 LMH, decreased rapidly to about 38 LMH, and then progressively increased back to 60 LMH. Investigations indicated that this was not due to any change in the nature of the feed, but was most probably due to a structural change in the membrane. This was concluded by examining the pure water fluxes. The PWF started off at about 100 LMH, increased rapidly to 350 LMH, decreased rapidly to 100 LMH and then slowly increased back to 300 LMH.

The pure water flux at a specified pressure can only increase if there is a change to the structure of the membrane. It is most probable that some irreversible chemical change has occurred due to either the caustic or some component of the waste caustic, causing the NF membrane to become more "open", resulting in a an increase in fluxes and a corresponding decrease in separation efficiency.

## SUMMARY OF MEMBRANE PERFORMANCE

The performance of the different membranes tested, in terms of the selected performance criteria, is summarized below :

| | **WFMF** | **CUF** | **TNF** |
|---|---|---|---|
| **Operating pressure, velocity** | 2 bar, 2 m/s | 1 bar, 1 m/s | 20 bar, 1 m/s |
| **Separation efficiency** | Inconsistent<br>Poor | Consistent<br>V good | Consistent<br>Excellent |
| **Fluxes** | Not determined | Average of 35 LMH with backflushing | 30 LMH to 60LMH |
| **Membrane Stability** | stable | stable | unstable |
| **Cleanability** | Not determined | V good with chemical cleaning | Not determined |

## ECONOMIC ASPECTS

From this study, the two systems that could be considered for caustic cleanup are CUF and TNF, since both give very promising removals of suspended contaminants. The choice of which system should be pursued further will thus depend on the relative economics. A detailed economic evaluation was beyond the scope of this project. However, the relative economics of the membrane systems may be inferred from the availability of membranes (i.e. local or imported), fluxes and operating conditions.

Comparative capital costs

The TNF modules are available in areas up to 2.6 $m^2$. The currently available CUF module has a membrane area of approximately 7 $m^2$. The fluxes obtained on TNF are up to 60 LMH, while that obtained on CUF is approximately 35 LMH. Hence, for a specified duty Q (L/h), the number of TNF modules required would be about 1.5 times the number of CUF modules required.

The TNF system would have to constructed of stainless steel, due to the high operating pressure. The CUF system is constructed of PVC, available locally.

Hence, even without detailed prices being available, it is clear that the capital cost of a TNF system would be greater than that of a CUF system, for a specified duty.

Comparative energy costs

The operating pressure for the TNF system is 20 times that of the CUF system. Hence, the energy requirements would be of a similar magnitude. There is not expected to be any significant difference in operator requirements, since both systems could be designed to be manually operated or fully automated. Hence, the operating cost for the CUF system is expected to be substantially lower than that of the TNF system.

Maintenance and module replacement

There is not expected to be a significant difference in maintenance of a TNF and CUF system. The replacement of membranes for the CUF system is expected to be less than the TNF system, in view of the fact that they are imported, and in view of the poor prevailing exchange rates.

Summary

In summary, both the capital and operating costs of the CUF are likely to be lower than that of the TNF system. In view of the fact that the separation efficiency of the TNF system is only marginally better than the CUF, it may be concluded that the CUF would be more economically attractive for caustic cleanup.

## CONCLUSION

WFMF gave a very inconsistent product quality, ranging from poor to very good. The system would not be suitable to clean up used caustic for reuse. In larger scale applications, however, it may be preferable to use WFMF to pretreat the waste caustic, prior to cleanup by CUF or NF.

CUF gave a very good product quality, from 1 NTU to 10 NTU, probably suitable for direct reuse. Average fluxes range from 35 LMH to 42 LMH, and could be maintained for up to 32 hours with regular backflushing. The membrane was stable to caustic, and fouled membranes could be recovered with chemical cleaning.

TNF gave an excellent product quality, generally around 1 NTU. However, the permeate fluxes and pure water fluxes were inconsistent and changed drastically with time. This is most probably indicative of a change in membrane structure, indicating possible instability when operated on waste caustic.

In considering economic aspects, the capital cost of a CUF system is likely to be significantly lower than a TNF system. The operating costs of the CUF system are also likely to be lower, due to lower operating pressures. Maintenance costs may not differ musch between CUF and TNF. Overall, therefore, the CUF system is likely to be more cost effective than a TNF system, while the TNF produces a higher quality of product.

## RECOMMENDATIONS

The following aspects need to be addressed further in order to progress to the industrialisation of a local membrane system for caustic reuse :

(i) Criteria for reuse of caustic – The project team were unsuccessful in obtaining from the beverage bottlers a clear indication of the criteria that recycled caustic must meet to be considered for reuse, seemingly because caustic reuse had not been given serious consideration previously. The caustic suppliers should have a better understanding of the criteria that caustic cleaning solutions must meet, but were reticent in revealing this information.

(ii) Economic evaluation – Ultimately, the cost of recycling caustic must be compared to the cost of using fresh caustic. This requires information on criteria for reuse, additives in the caustic solution, and the cost of fresh caustic and additives. Once again, this information could not be obtained from the bottlers.

(iii) Performance in batch concentration mode – The permeate fluxes obtained in this study were obtained by operating in a constant concentration mode. This will simulate the situation where a side stream is continuously drawn off from the bottle wash bath and cleaned. Alternatively, the caustic cleanup could be done in a batch concentration mode. Design fluxes for this mode cannot be inferred from this study, but can easily be obtained experimentally.

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# 1 INTRODUCTION

## 1.1 Background to the project

Sodium hydroxide solution (caustic) is widely used as a cleaning agent in the food and beverage bottling industries. The two main uses are as a cleaning-in-place (CIP) solution and in bottle washers.

In CIP applications, a caustic solution with a strength ranging from 5 % to about 20 % is used, depending on the industry. The caustic is recirculated through the vessel to be cleaned, and returned to a storage tank. During the clean, the caustic solution picks up suspended solids, organics, silicates etc., and hence deteriorates with each clean. The CIP solution is usually used for four to eight cleans before being discarded to drain. The criteria for dumping differs from industry to industry.

In the bottle washing process, the bottles are firstly plunged into a caustic bath ( 2 % to 5 % caustic strength). The bottles are then drained and allowed to dry (with warm air in some instances). The bottles then enter a series of three rinse baths, which are operated in a counter current mode. The caustic bath serves to remove residual labels, glue, grit, residual dehydrated organics etc from the bottles, and hence this bath progressively becomes contaminated with these. When this contamination reaches an unacceptable level, the entire contents of the bath are dumped. In some bottling plants, an attempt is made to extend the life of the caustic by periodically pumping the contents into a settling tank, allowing the grosser solids to settle out, and returning the supernatent to the bath. The rinse baths remove any residual caustic from the bottles, and prepare them for filling. The carryover of caustic from the caustic bath to the rinse baths is not very high, but increases as the level of contamination in the caustic bath increases. In general, there is a very low concentration of caustic in the effluent from the rinse baths.

Thus, there are three main sources of caustic effluents from food and beverage bottling plants:

(i) spent caustic from CIP. This has a relatively high concentration of caustic, contaminated with suspended and some soluble contaminants

(ii) spent caustic from the bottle washer caustic bath. This has a relatively high concentration of caustic, but is contaminated with suspended and some soluble contaminants.

(iii) effluent from the rinsebaths. This is a very dilute caustic stream.

It must be noted that for CIP and bottle wash bath effluents, the caustic strength of the waste caustic stream is still high, and the stream is discarded solely because of the level of contamination. If the level of contamination is reduced, the effective lifespan of the caustic solution could be extended significantly, implying a significant savings in caustic usage.

Conversely, the effluent from the rinsebaths is very dilute. Here, the effluent streams would have to be cleaned up and concentrated up, if the caustic is to be reused.

Internationally membrane-based systems for the cleanup and reuse of spent caustic solutions are readily available from various commercial vendors. ZM Environmental Systems (www.zmtech.com) uses a nanofiltration or ultrafiltration membrane to remove suspended and dissolved solids, and procuse clean caustic for reuse in the peeling and sanitizing industries. PCI-Memtech (www.pci_memtech.com) produces a tubular nanofiltration membrane for spent caustic recovery. A ceramic membrane for caustic cleanup is produced by FES International (www.fesintl.com). The AlkaSave system uses nanofiltration modules produced by Koch (www.kockmembrane.com).

In South Africa, however, cleanup of spent caustic solutions and their subsequent reuse or recycling is rarely practiced. One reason is that spent caustic solutions have not been regarded as a problem. The practise of neutralization and disposal has been widely applied. This is likely to change as environmental legislation is tightened up and cleaner production philosophies become more popular. The other reasons for the lack of membrane based caustic recycling locally include :

(i) The high cost of imported caustic cleanup systems

(ii) The high cost of obtaining spares and new membranes for imported systems

There is also the perception that membranes are a very "high tech" technology that requires very high skills levels to operate and maintain. This is exacerbated by the lack of a local expertise base to support these systems in terms of operations, optimization, modifications etc.

There could be considerable benefit to the South African food and beverage industry and the broader aspect of environmental protection, therefore, if a locally developed caustic cleanup system was available which addressed the above concerns. This forms the overall objective of this project.

## 1.2 Objectives

The specific objectives of the project are as follows :

(i) to develop a management strategy for caustic streams in the beverage bottling industry

(ii) to develop a viable membrane-based system for the reuse and/or recovery of used caustic solutions, and to demonstrate this to potential users

(iii) to develop a human resource skills base that is capable of implementing such processes in industry

(iv) to develop a commercialisation strategy for the proposed processes

In view of the fact that off-the-shelf systems are available overseas, and in consideration of the factors that make local industry reticent to use those systems, the overall "guiding principles" for the project are :

(i) draw on existing South African membrane technology where available

(ii) where South African technology is not available focus on membranes and modules that are readily available internationally, and where the vendor is prepared to supply modules for inclusion in a locally constructed system. This latter point is of significance since it is known that various vendors are only prepared to supply full systems, and not individual modules.

## 1.3 Performance Criteria

In order for a membrane caustic recovery process to be attractive to users, it must be able to reduce the level of contamination in the waste caustic to "adequate" levels, it must be economically cost-effective, and it must be reliable and easily operable. The definition of "adequate" would be dependant on the application, and would be defined by the user.

Accordingly, the performance criteria determined for each membrane system were :

(i) separation efficiency

(ii) permeate fluxes

(iii) resistance to caustic.

(iv) cleanabilility of the membranes.

The separation efficiency was determined from turbidity and suspended solids measurements on the feed and permeate. Resistance to caustic was determined by monitoring whether there was any change in pure water flux and rejection, when the membrane was exposed to caustic. Cleanability of the membranes was determined by assessing whether the fluxes could be easily recovered after many runs.

## 2 LITERATURE AND INTERNET SURVEY

A literature search was performed to identify previous membrane based processes used for caustic cleanup as well as caustic concentration. The databases surveyed were Waterlit, Emily, SA Cat, and SA Citations. The keywords used for the literature were *sodium hydroxide recovery*, *caustic soda*, *membrane processes/systems* and *caustic recovery*. No significant information on membrane systems for caustic cleanup were obtained. The one process that was found concerned the concentration of dilute caustic solution, and was developed by the Pollution Research Group, University of Natal. The system combines neutralisation together with three standard membrane techniques:- cross-flow microfiltration, nanofiltration and electrochemical recovery. In addition, the options of reverse osmosis or evaporation was considered as an effluent concentration step.

In the internet search, however, numerous advertisements for caustic cleanup systems based on membrane processes were found, indicating that these systems do exist but seeming have not been reported in research literature. These systems use a microfiltration (MF) or ultrafiltration (UF) system to remove suspended and colloidal contaminants from caustic. This may be followed by a nanofiltration (NF) step to remove small molecular weight organics.

Whilst the internet survey indicate that there were various processes for the cleanup of caustic, sparse information was obtained on concentration of dilute caustic streams. Various membrane suppliers were contacted to establish whether they had membranes capable of concentrating up dilute caustic. PCI Membranes in England was visited by a member of the project team in 1999, and this issue was raised with their technical personnel. From all of this it emerged that commercial suppliers of reverse osmosis membranes are extremely reticent about using their membranes/modules on caustic. While membranes that specifically concentrate sodium do exist (Nafion), they are extremely expensive, and would not be viable in large volume applications.

What emerged therefore, was that :

(i) systems for the cleanup of caustic (without concentration) are readily available and have been widely tested. They use MF or UF to remove suspended solids and colloids, possibly followed by NF for small organics.

(ii) systems for the concentration of caustic streams using membranes is not viable at present.

Hence, the project would limit itself to processes for the clean-up of caustic streams, i.e. spent CIP and bottle wash bath effluent, and will not consider the concentration of rinse bath effluent.

# 3 MEMBRANES AND TEST SUSPENSIONS

## 3.1 Choice and Procurement of Membranes

South Africa had two locally developed membrane technologies :- MF and UF. The MF technology is the woven fibre microfilter (WFMF) developed at the University of Natal, and fabricated by Gelvanor. Two UF technologies are available. Tubular UF (TUF) was developed by the Institute of Polymer Science, University of Stellenbosch, and is manufactured by Envig. Capillary UF (CUF) was also developed by the Institute of Polymer Science, and is available from FiltRsa. It was decided that WFMF and CUF would be the first choices for MF and UF test membranes.

South Africa does not however have any locally developed NF or RO technologies that could be used to remove very fine organics. Following on from the internet survey, various overseas membrane suppliers were identified as possible suppliers of caustic resistant NF membranes. Firstly, attempts were made to obtain further information and membranes via their local agents. This did not prove successful, with most of the local agents referring queries to their overseas principals. Next, various overseas suppliers were contacted via email to obtain further data on their systems. However, in almost all instances, communication from the supplier ceased when it was realized that this was not a commercial enquiry.

The only company that proved helpful was PCI Membranes in England, following a visit from a member of the project team. They indicated that they would be prepared to supply membranes and modules, and would not insist on supplying systems. One of their NF membranes had apparently been used in caustic cleanup. After various negotiations, they supplied a set of test membranes (NF) at no charge.

The membranes chosen as test membranes are summarized in the Table 1.

Table 1 – Details of membranes evaluated in the study

| Membrane Type | Supplier and Description | MW Cutoff / Rejection | Size |
|---|---|---|---|
| MF | Gelvanor<br>Woven fibre polyester | N/a | 25 mm diameter, variable length |
| UF | FiltRsa<br>Capillary UF, polysulphone, #1713 | 35 000 | 1.2 mm capillaries, variable length |
| NF | PCI<br>Tubular NF, type AFC30, polyamide film | 75 % $CaCl_2$ | 12.5 mm diameter tubes, length 1.2 m |

## 3.2 Test suspensions

Two sources of waste caustic were initially identified as test suspensions :

(i) Waste CIP from the sugar industry, supplied by the Sugar Milling Research Institute (SMRI), Durban. The fresh CIP has a caustic strength of approximately 20 %. The main use in in the cleaning of evaporators. The caustic is used for 4 to 8 weeks before being discarded. A batch is dumped when the viscosity increases to the point where pumping becomes difficult.

(ii) Bottle wash bath effluent from ABI, Phoenix (Durban). This has a caustic strength of about 1 % to 5 % . The batch is used for 8 weeks to 10 weeks before being discarded. Samples were obtained directly from ABI, Phoenix.

The project commenced with the evaluation of WFMF for the cleanup of the sugar waste caustic. It progressively emerged, however, that there were various problems associated with using this test suspension. These included :

(i) vast differences between batches of waste caustic

(ii) difficulties with obtain regular test samples. All test samples had to be obtained directly from SMRI, and could not be obtained directly from the refineries. Our contact person at SMRI changed thrice due to resignations, and this eventually impacted negatively on communications.

(iii) A lack of clear direction as to what we were supposed to achieve. For example, we were informed that spent caustic was dumped when the viscosity reached a certain value. However on a visit to Illovo sugar in Mtubatuba a member of the project tea was told that this was not so. Three different caustic concentrations are used, 30 %(new), 20 % and a low concentration caustic( 2 %), each with a different cleaning application. The concentrated caustic is made up as required. When the concentrated solution is "spent", it is diluted for use in the other cleaning applications.

It then emerged that SMRI was initiating its own investigations into the use of membranes for caustic cleanup. The project team then decided to cease investigations on the sugar spent caustic, and to focus on the bottle wash caustic from ABI. Accordingly, the UF and NF investigations were performed on the ABI caustic only.

# 4 EXPERIMENTAL

Four experimental rigs were employed in this study, viz. flat-sheet batch filtration, woven fibre crossflow microfiltration, tubular nanofiltration and capillary ultrafiltration. These are described below.

## 4.1 Flat-sheet rig

The flat-sheet rig is a cylindrical stainless steel vessel of volume 400 ml. The vessel comprises of two sections locked together by two bolts. The upper section has a volume of 400 ml and serves as the feed tank. It is fitted with a magnetic stirrer. The bottom section is merely a steel base within which is a porous plastic disc of diameter 76 mm. When the base of the vessel is separated from the main cylinder by opening the two bolts, this allows one to place any type of flat sheet filters onto the porous plastic disc. An O-ring is used to keep the filtering discs in place and this ring also acts as a sealant when large pressures are applied to the contents of the vessel. In these experiments the filtering discs were cut from flat sheet woven fibre microfiltration cloth and flat sheet ultrafilters. The side of the bottom section of the vessel has an outlet through which permeate is collected. The vessel is rendered leak-proof when the bolts are fastened.

The upper section of the vessel has two openings drilled into it. The first opening is used to introduce a fixed amount of feed into the vessel. Fastening a bolt into it seals off the opening. The second opening allows for the connection of an airline to it. Compressed air can then be used to force the feed in the system through the filtering medium. The pressure in that airline is regulated using a standard gas cylinder regulator. The first opening can also be used to fit in a pressure gauge thus recording the pressure within the vessel.

Before start up an inspection of the equipment was made to ensure proper functioning and that there were no air leaks. The feed was placed into the tank. The airline was connected to the vessel and the desired pressure obtained by adjusting the regulator. Within seconds permeate exited the vessel and was collected in a permeate tank for analysis. Once all of the feed eluted the vessel the air supply was cut off and the vessel was cleaned and prepared for the next set of experiments.

## 4.2 Crossflow Microfiltration (CFMF) Rig

The CFMF system has three fifty-liter tanks inter-connected to each other by polyvinyl chloride piping. There is a feed tank, a precoating tank and a wash tank. The feed tank is fitted with a cooling coil that maintains the feed temperature within a specified range. Each tank is fitted with a mixer. The tanks were assembled together such that independent usage as well as drainage could be achieved. Placing valves at specific locations on the piping network accomplished this. The tanks are all connected to a single suction point from which positive displacement pump draws raw effluent or the pre-coat suspension and pumps this into the CFMF tube. The speed of the motor and hence the pumping rate is controlled by a speed controller. The control mechanisms (for pump protection) that are incorporated into the design are high-pressure and low-level cut-offs.

The pump discharges feed into a 25 mm diameter WFMF tube. Permeate from the tube drains into a plastic permeate gutter from which it could be returned to any of the tanks or removed from the system. The reject from the WFMF tubes is returned to the feed tank. A diaphragm valve located on the reject line controls the pressure in the tubes. The rig is designed to also operate in a precoat, feed and wash cycle. This is achieved by simply ensuring that the pump is drawing from the required tank. At the end of the experiment the system is washed with water (adequate cleaning strategy) and prepared for the next run.

### 4.3 Crossflow Nanofiltration (CFNF) Rig

The Nanofiltration rig has three one hundred liter tanks inter-connected to each other by stainless steel piping. There is a feed tank, a permeate tank and a wash tank. The feed tank is fitted with a cooling coil, which maintains the feed temperature within range. Each tank can have a mixer fitted to it. The feed and wash tanks are assembled together such that independent usage as well as drainage could be achieved. Placing valves at specific locations on the piping network accomplishes this. The feed and wash tanks are connected to a single suction point from which a centrifugal pump (fitted with a motor) draws feed and pumps this into the nanofiltration tube. The speed of the motor and hence the pumping rate is controlled by a speed controller. The control mechanisms (for pump protection) that are incorporated into the design are high-pressure and low-level cut-offs.

The pump discharges feed into a 12.5 mm diameter nanofiltration tube. Permeate from the membrane drains into a plastic collecting tube holder around the membrane from which it could be returned to any of the tanks or removed from the system via a polyethylene hose. The reject from the nanofiltration tube is returned to the feed tank. A needle valve located on the reject line controls the pressure in the tubes (up to 50 bar). The rig is designed to operate in a feed and wash cycle. This is achieved by simply ensuring that the pump is drawing from the required tank. At the end of the experiment the system is washed with water (adequate cleaning strategy) and prepared for the next run.

### 4.4 Capillary Ultrafiltration (CUF) Rig

The capillary rig consists of a feed tank, pump and capillary membrane module. The pump draws feed from the feed tank and pumps this into the capillaries. The required backpressure in the capillaries is obtained by adjusting the diaphragm valve located on the reject line, which empties into the feed tank. The permeate can be returned to the feed tank or collected in a separate vessel and analyzed.

# 5 EVALUATION OF WOVEN FIBRE MICROFILTRATION

WFMF trials were conducted on spent caustic soda samples were obtained from the SMRI, using both the flat-sheet and crossflow rigs. Typical analysis of the spent caustic is shown in Table 2. According to SMRI personnel, caustic soda is reused until the viscosity reaches the level where it can no longer be pumped. The objective in treatment was to reduce the viscosity so as to enable extended use of the caustic soda.

Table 2: Overall analysis of feed sample as provided by SMRI

| Species | % (m/m) |
|---|---|
| NaOH | 26.9 |
| $Na_2CO_3$ | 3.6 |
| $SiO_2$ | 2.4 |
| $PO_4$ | 0.52 |
| CaO | 0.25 |
| $K_2O$ | 0.11 |
| $Fe_2O_3$ | 0.04 |
| MgO | 0.03 |
| Water/Organic | 66.2 |
| Total | 100 |

## 5.1 Identification of contaminants contributing to the high viscosity

The first task was to identify which of the components contributed to the significant increase in viscosity. Initially it was suggested that this was due to the carbonates and silicates in the system.

To test this, a solution of sodium hydroxide, sodium hydrogen carbonate and sodium bicarbonate containing the same ratio as indicated in Table 1 was prepared and left to stand for a period of time. It was found that this was vastly different from the sample obtained from SMRI. The solution was significantly less viscous than the sample of caustic obtained from the SMRI.

The conclusion reached was that the viscosity increase was not due to the carbonates but could be due to the organic contaminants as these were not added to the solution.

## 5.2 Development of analytical techniques

The next stage was to focus on establishing reliable analytical techniques for the system i.e. quantifying the concentrations of sodium hydroxide, sodium hydrogen carbonate, sodium bicarbonate and total organic content. This would be used to evaluate the performance of the microfiltration membranes.

### 5.2.1. Sodium species

Analytical techniques to determine NaOH, $Na_2CO_3$, $NaHCO_3$ concentrations were established with the aid of the analytical chemistry department and the SMRI. It was then decided to determine the reliability of these tests. A test solution was prepared and the analysis for the sodium species was carried out. It was found that the experimental values obtained for the various sodium species did not tally with the actual concentrations. After much repetitions of the analysis, it was decided to consult a private consultant, ChemScience Laboratories.

It was found that the analytical techniques were reliable and the discrepancies were due to the constituents of the test solution. The problem was due to us using three basic components (NaOH, $Na_2CO_3$, $NaHCO_3$) and trying to determine their concentrations. Due to the high pH and the high concentration of NaOH, only two of the three species would exist in solution. That is the $NaHCO_3$ would be converted into $Na_2CO_3$ using NaOH. Thus by adding $NaHCO_3$ to the sample resulted in a decrease in NaOH concentration and an increase in $Na_2CO_3$ concentration.

### 5.2.2. Organics

Since it seemed that low concentrations of organic material could be the major contributor to the increase in viscosity, a concerted effort was made to determine the organic content and constituents of the spent caustic. Two methods were proposed, viz. HPLC and TOC.

Consulting with analytical chemists at M L Sultan indicated that due to the high concentration of NaOH, the HPLC could not be used as it would damage the column. Similar problems were experienced with attempts to measure TOC. In the greater Durban area, none of the laboratories contacted were prepared to do the analysis, since concentrated caustic is too corrosive. The option of dilution was discarded since significant dilution is required and the organics would fall below the detection limits of the instruments.

After spending quite some effort on attempting to quantify organics, it wa eventually decided that this was not easily achievable. The project team then decided to revert to viscosity measurements as the indication of effectiveness of cleaning the spent caustic.

## 5.3 Preliminary microfiltration tests on flat-sheet test cell

Preliminary tests were conducted using the flat sheet test cell to determine the efficiency of WFMF to clean up spent caustic. A microfiltration membrane was obtained from the curtain supplied by Gelvenor. The experiments were conducted in dead-end mode at a pressure of 100 kPa.

With the assistance of the SMRI, the feed, permeate and cake samples were analysed for NaOH and $Na_2CO_3$ concentrations, total dissolved solids, minerals and viscosity. This is shown in Table 3.

Table 3: Analysis of the feed and permeate samples from flat sheet WFMF rig

| | **Feed** | **Permeate** |
|---|---|---|
| Dry solids [ % ] | (34.30) | (35.18) |
| Sulphated ash [ %] | 14.70 | 13.58 |
| Caustic strength [ % NaOH ] | 25.10 | 21.98 |
| Viscosity @ 25 $^{o}$C [ cP ] | 17.2 | 7.1 |

These results were very promising. Whilst there was a minor reduction in NaOH concentration (25.1–21.98) there was a significant decrease in viscosity. The SMRI and Tongaat-Huletts were extremely thrilled with the reduction of viscosity. The viscosity of pure NaOH at the same caustic concentration at 20$^{o}$C is 5.75 cP. The WFMF system was able to reduce the viscosity to near its original value.

## 5.4 Trials on Crossflow Microfiltration rig

The next stage was to evaluate CFMF. Trials on CFMF were initiated in August 1999, on a sample of caustic obtained from the SMRI. The caustic sample was taken from the middle of its life-cycle.

The feed consisted of supernatent only, i.e. the samples were allowed to settle in their containers and the supernatent was carefully poured off. The viscosity of the feed was 10 cP. For the first 17 minutes the pressure was maintained at 50 kPa and the tube velocity set to 0.5 m/s. Thereafter the pressure was increased to 200 kPa and the velocity was increased to 2 m/s.

It was found that the viscosity of the permeate started at a low value of 4.32 cP and increased to 8.5 cP after 3 hours of operation. During the first 17 minutes the viscosity increased from 4.32 cP to 6.72 cP. Two minutes after increasing the pressure to 200 kPa, the viscosity of the permeate was 7.39 cP.

The low feed viscosity is due to the fact that only the supernatant was used. Further, the sample of the feed was taken from the feed tank and the low viscosity may also be due to the water contained in the lines/pipes, which mixed with the supernatant. The initial low viscosity of the product could also be due to dilution from residual water in the piping. However the subsequent increase in viscosity on increasing the pressure was unexpected. This indicated the possibility that the fouling layer may be gel-like, and was being forced through the tube wall at higher pressures.

Due to the limited amount of sample available, as well as the spurious effects introduced by the large dead volume in the crossflow rig, it was decided to revert to experimentation on the flat sheet test cell.

## 5.5 Further Trials on the Flat Sheet WFMF

### 5.5.1. Replicability of previous performance

The objective here was to determine whether the excellent results obtained in the preliminary trials were replicable.

A sample of mixed feed (i.e. the suspension was well mixed) was filtered using the flat sheet cell with a woven fibre microfiltration membrane. The operating pressure was 200 kPa.

The feed viscosity was 19.2 cP, while the viscosity of the combined permeate was 13.2 cP.

This result indicated that the microfilter was able to reduce the viscosity significantly. However this result differ significantly from the initial test conducted in 1999, where the viscosity was reduced from 17.1 cP to 7.1 cP. The difference between these two tests was operating pressure (200 kPa in this test, and 100 kPa previously). Hence, it was decided that the effect of pressure should be investigated.

5.5.2. Effect of Operating Pressure

Two feed samples were used - a mixed feed, and a supernatent. For each feed a series of runs were performed at different operating pressures. The results are presented in Table 4 below.

Table 4 – Viscosity Change in Flat Sheet WFMF

| ***Feed Type*** | **Mixed** | **Supernatent** |
|---|---|---|
| ***Feed Viscosity*** | 15.12 | 12 |
| | **Combined Permeate Viscosity (cP)** | |
| **Operating Pressure** | | |
| 60 | | 7.97 |
| 100 | | 9.12 |
| 160 | | 10.08 |
| 200 | | 10.68 |
| | | |
| 75 | 11.52 | |
| 150 | 11.04 | |
| 190 | 11.8 | |
| 200 | 8.76 | |

In experiments on the supernatent only, there is a progressive increase in permeate viscosity as the operating pressure is increased. This seems to indicate that the foulants are most probably forming an unstable gel-like fouling layer that is being forced through the membrane at higher pressures. For the runs on the mixed feed, ther is no clear trend with operating pressure.

Overall, however, the permeate viscosities are much higher than that obtained in the preliminary test. This could possibly be due to a difference in the nature of the feed. In the preliminary test, the feed sample was obtained at the end of the caustic life-cycle, i.e. just before the caustic could be dumped. This would obviously have a high concentration of contaminants, as indicated by the high viscosity of 17.1 cP. The sample used in all the above experiments was obtained near the middle of the caustic life-cycle, and accordingly has a lower viscosity (15.2 cP). It could occur that as the concentration of contaminants increases, a more stable fouling layer forms, yielding a better performance on the microfilter.

#### 5.5.3. Effect of Precoating

In general, precoating a woven fibre microfilter increases it retention capabilities. The effect of precoating the microfilter with powdered activated carbon (PAC) and limestone was investigated.

For the PAC, a suspension of 15 g/l in water was made up, and the microfilter disc was precoated with this at a pressure of 100 kPa. The feed sample was then introduced into the cell and filtered at 200 kPa. For the PAC trial, only the supernatent was used.

The results were as follows :

| | | |
|---|---|---|
| Feed Viscosity (supernatent) | = | 11.04 cP |
| Permeate Viscosity | = | 10.56 cP |

For the limestone experiment, a suspension of limestone (KULU 5) and water was made to a concentration of 15 g/l. The microfilter was pre-coated using a pressure of 200 kPa. The feed sample was then introduced, and filtered at a pressure of 200 kPa. For the limestone trials, both supernatent and mixed feed were investigated.

These results were as follows :

| | | |
|---|---|---|
| Feed Viscosity (supernatent) | = | 11.04 cP |
| Permeate Viscosity | = | 10.56 cP |

| | | |
|---|---|---|
| Feed Viscosity (mixed feed) | = | 16.32 cP |
| Permeate Viscosity | = | 11.04 cP |

The above indicated that precoating the microfilter did not yield any significant improvement in performance.

## 5.6 Summary

Initial trials using WFMF on CIP waste from the sugar industry indicated that the microfilter was capable of reducing the viscosity down to acceptable limits. However, this performance could not be obtained consistently and repeatibly. In all trials, WFMF did effect some reduction in viscosity, but this was generally inadequate for reuse. The effects of varying the operating pressure and the effects of precoating the filter were also investigated. Precoating did not achieve any significant improvement in performance.

It must be concluded that WFMF alone is inadequate to recycle spent CIP solution from the sugar industry.

However, WFMF could play a role as a pretreatment step, if it is found that an expensive or exotic membrane is necessary to remove the target contaminants that contribute to the viscosity increase. In this instance, the WFMF could remove the grosser contaminants and thus extend the life of the expensive membrane.

# 6 EVALUATION OF ULTRAFILTRATION

All the ultrafiltration trials were conducted on spent bottle wash solution obtained from ABI. Preliminary trials were conducted using the flat sheet rig, and these were followed by trials on the CUF rig.

A major problem was experienced with establishing criteria for the reuse of spent caustic. Various enquiries to various personnel at the ABI site proved negative, since it seemed that recycling the spent caustic had not really been given serious consideration previously.

The fresh caustic includes various proprietary additives to reduce foaming etc. The spent caustic is contaminated with suspended material and probably some organics. It is easy to quantify the suspended material, but more difficult to quantify the organic content. The approach taken by the project team was to assume that the major contaminant was the suspended solids. The objective would then be to determine whether the suspended solids could be reduced to very low levels. If/when this is achieved, the product (cleaned) caustic would have to be tested by the user to establish whether its cleaning characteristics are similar or different to the fresh caustic.

### 6.1 Flat-sheet Trials

Caustic samples were collected every two weeks (over an eight week in-use cycle) from ABI. These samples were filtered in a test cell at 1 bar using a flat sheet UF membrane as the separating barrier. The flat-sheet UF membranes were obtained from the Institute of Polymer Science, University of Stellenbosch, and were cut into disks from the flat sheet cell. The flat sheets had a similar molecular weight cutoff to the capillary UF membranes (35 000).

To determine separation suspended solids measurements were made. The results of these preliminary trials are shown in Figure 1.

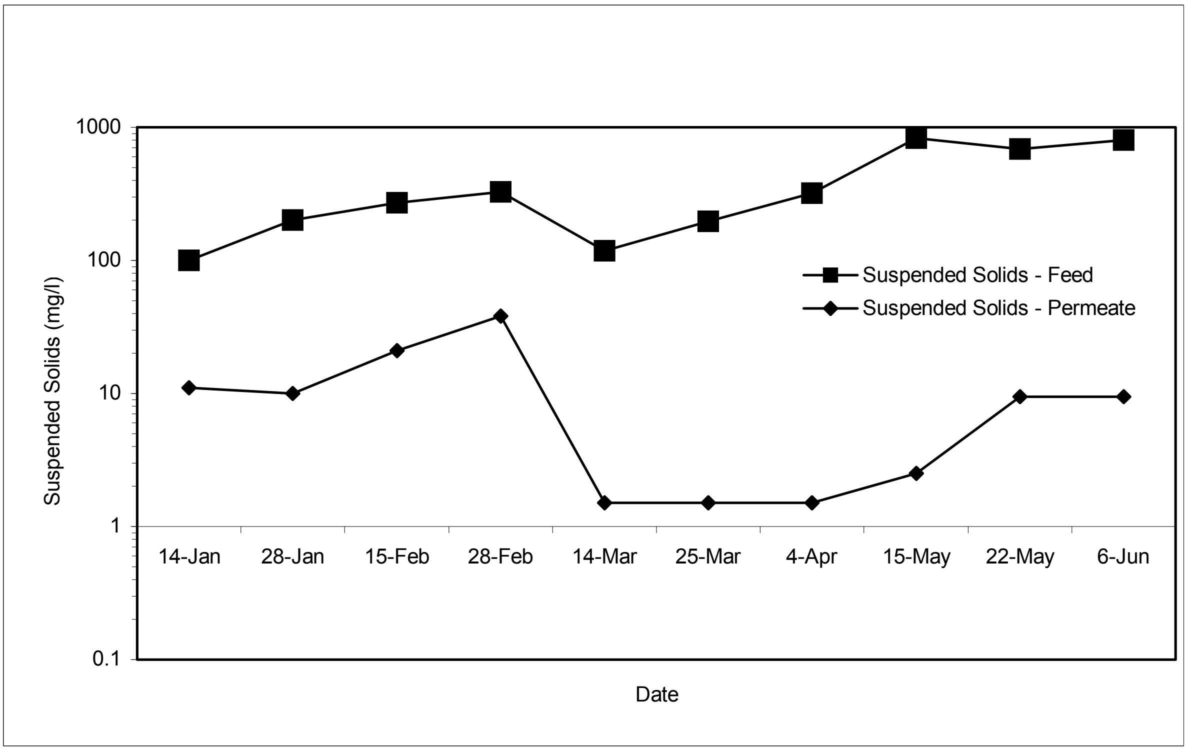


**Figure 1 - Removal of Suspended Solids : Flat-sheet UF Rig with ABI Caustic**

It can be seen that there was an excellent removal of suspended solids, with rejections ranging from about 90 % to over 99 %. This indicated that UF was possibly well suited to cleaning up bottle wash caustic. Note that two batches of caustic are depicted in the above figure. It can be seen that the suspended solids content of the batch increases by a factor of up to 9, during the life of the batch.

## 6.2 Capillary UF Trials

The waste caustic is pumped from a 5-litre storage tank via a peristaltic pump into the capillary module, which comprises 20 capillaries, each with a length of 0.22m and inside diameter of 0.0012 m. A diaphragm valve downstream of the module was used to regulate the operating pressure. A glycerine-filled pressure gauge is located between the module and the diaphragm valve to monitor the pressure in the line. 30 ml samples of permeate were collected periodically for analysis. The remainder of the permeate and the concentrate were returned to the feed tank. The system was thus operated in an approximate constant feed concentration mode.

All runs reported here were conducted at a pressure of approximately 1 bar, and at a tube velocity of 1 m/s.

### 6.2.1. Turbidity Rejection

In the flat-sheet ultrafiltration experiments it was seen that the permeate turbidities ranged either around 1 NTU or around 10 NTU, depending on the batch of caustic that was used. A similar phenomenon was observed in the CUF trials. Subsequent investigations indicated that the turbidity removal was very dependant on the age of the waste caustic. Permeate turbidities for an batch of caustic that had been in use for about 8 weeks is shown in Figure 2. Turbidities for a batch that had been in use for about 4 weeks is shown in Figure 3.

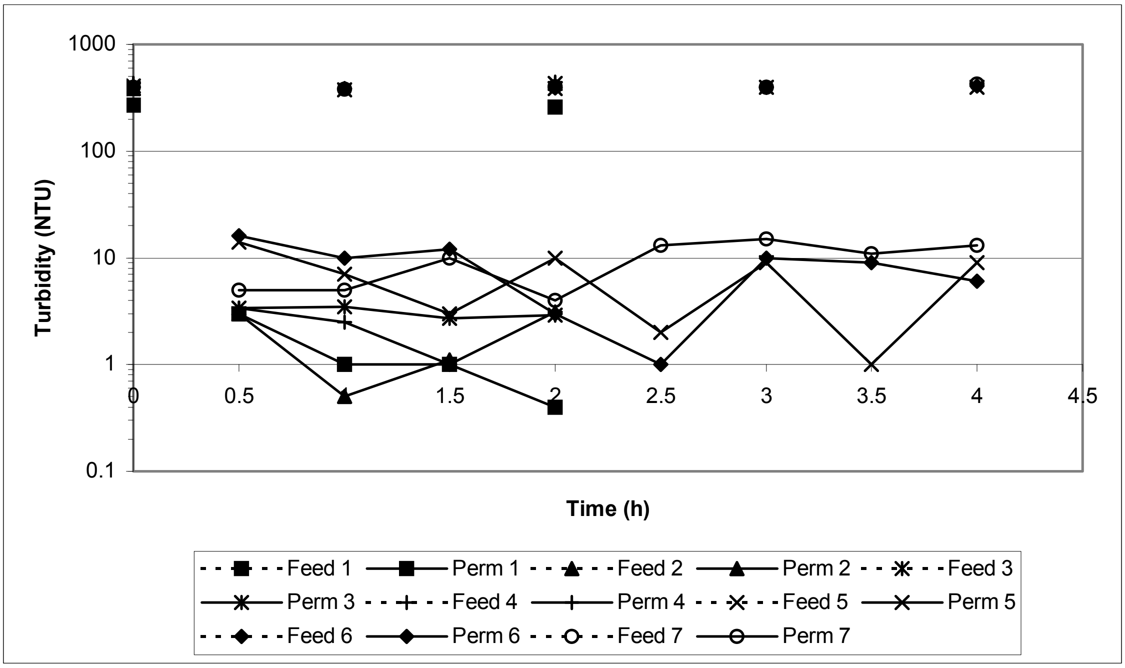


**Figure 2 - CUF turbidities obtained on a batch of waste caustic that was 8 weeks old**

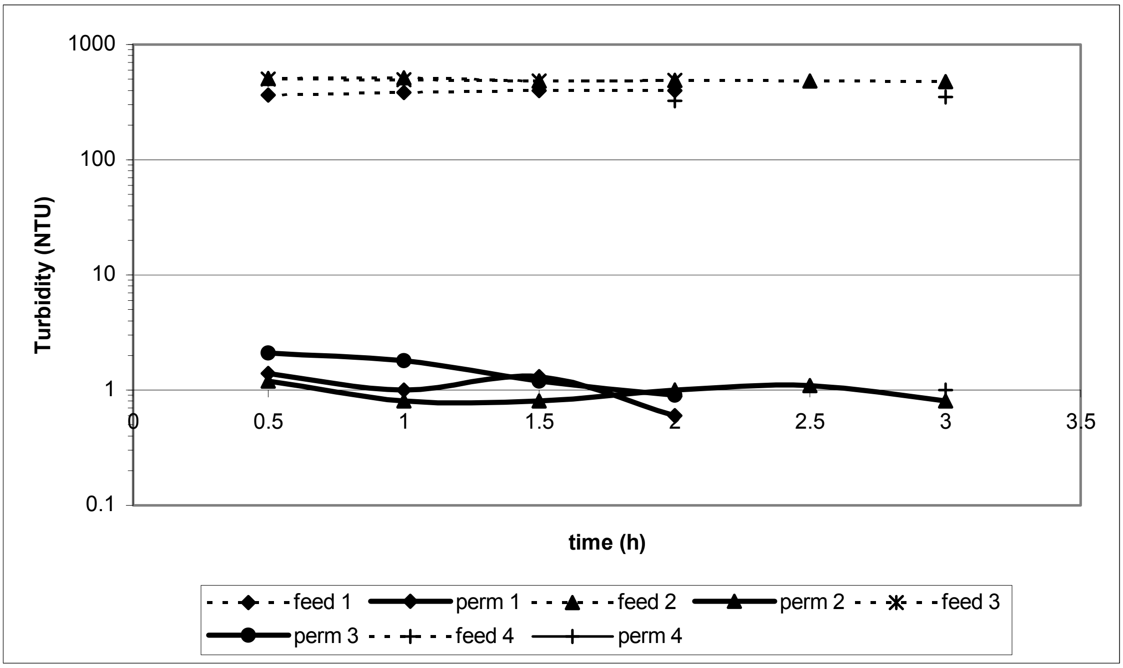


**Figure 3 - CUF turbidities obtained on a batch of waste caustic that was 4 weeks old**

It emerges clearly that the turbidity removal decreases with the age of the waste caustic. This is logical, since it would be expected that the amount of organic contaminants would increase with increased usage of the caustic.

Despite the above, however, the turbidity removal is still very good. In the instance of caustic that had been in use for up to 4 weeks, final turbidities < 2 NTU are achieved for feed turbidities ranging from 300 NTU to 500 NTU. In the instance of old caustic, final turbidities of around 10 NTU are achieved for feed turbidities around 400 NTU to 500 NTU. From the point of turbidity removal, therefore, the CUF process is capable of removing most of the suspended material in the waste caustic, enabling reuse of the caustic.

6.2.2. Permeate Fluxes

Typical permeate flux profiles for three different batches of caustic are shown in Figure 4. These were obtained with a tube velocity of 1 m/s, and an operating pressure of 1 bar.

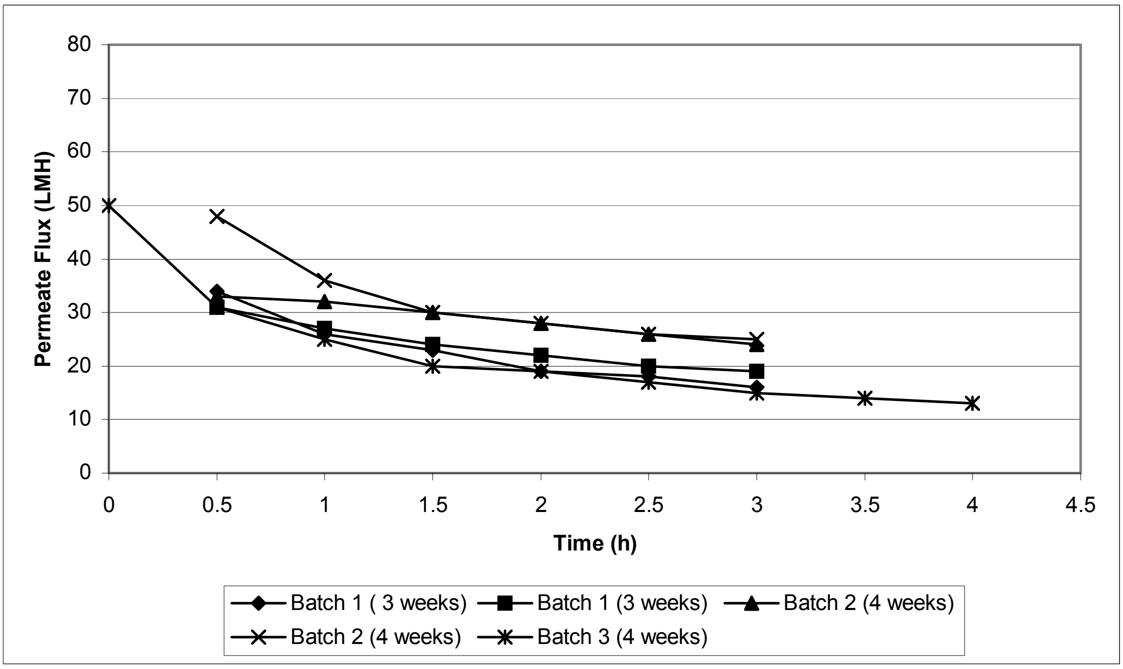


**Figure 4 - Typical flux-time profiles obtained on CUF of waste caustic**

In the above runs, permeate fluxes start off at around 50 LMH to 60 LMH. There is a rapid decrease in the first hour, down to 25 LMH to 35 LMH. This is followed by a slower decrease to 18 LMH to 23 LMH after 3 hours.

The fluxes obtained on the same batch of caustic are fairly repeatable. Batch 2 had been in storage for a few months, while Batch 3 was newly obtained. It is seen that there is a difference in the permeate fluxes obtained, although both batches had been in use online for the same period (4 weeks).

Backflushing, i.e. periodically reversing the direction of flow through the membrane, is commonly used as a means of flux enhancement. During backflushing, the clean water is pumped from the shell side through the walls of the capillaries, and into the capillary lumens. This flow serves to remove some of the accumulated fouling layer, which is exits in the concentrate. The effectiveness of backflushing in the current system was investigated. A typical flux-time plot with backflushing is shown in Figure 5. Here, the system was backflushed for 15 minutes after every hour and half of filtration time.

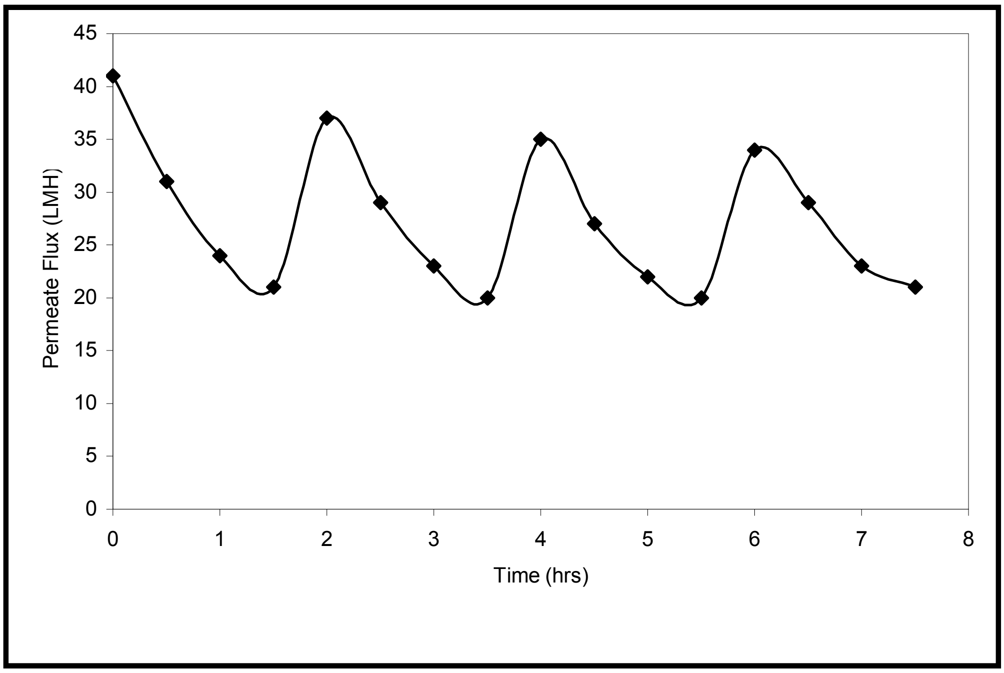


**Figure 5 - Effect of backflushing on permeate flux profile**

On comparing Figures 4 and 5, it is clear that backflushing is very effective in maintaining the permeate flux. In the above example, the backflushing period was 20 minutes. Investigations into the effect of backflushing period on backflush efficiency were performed. It emerged that backflushing for 5 minutes, followed by flushing out the system for a further 5 minutes, was as effective as backflushing for 20 minutes. This was adopted as the backflush strategy in subsequent investigations.

The effect of feed age on backflush efficiency was investigated on waste caustic obtained adter 3 weeks, 4 weeks and 6 weeks of utilisation respectively. The results are shown in Figures 6 to 8.

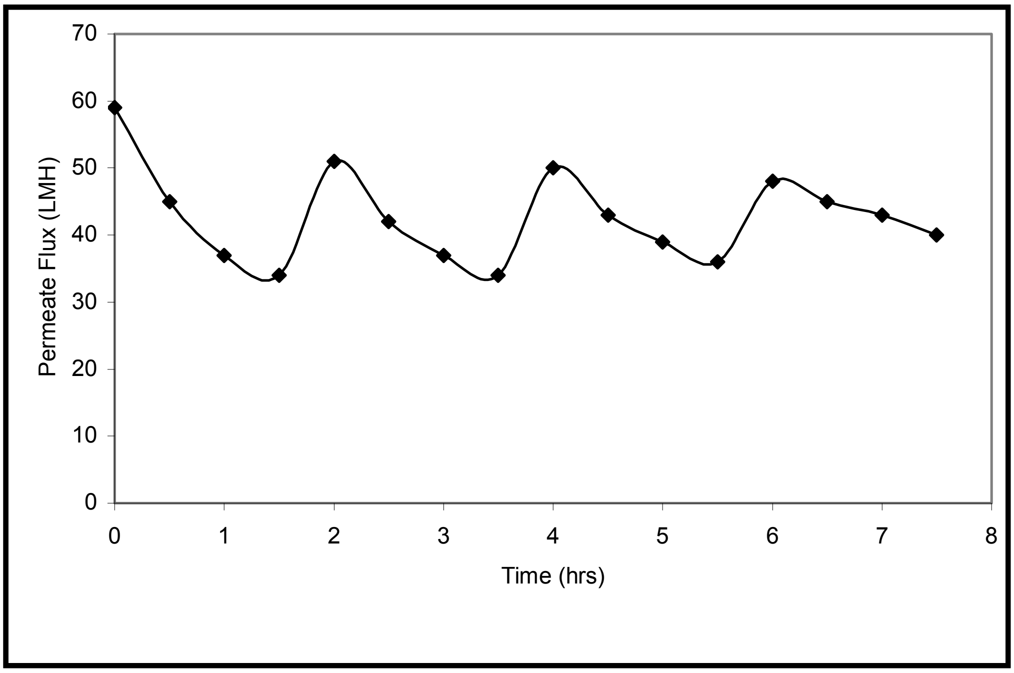


**Figure 6 - Effect of backflushing : feed age of 3 weeks**

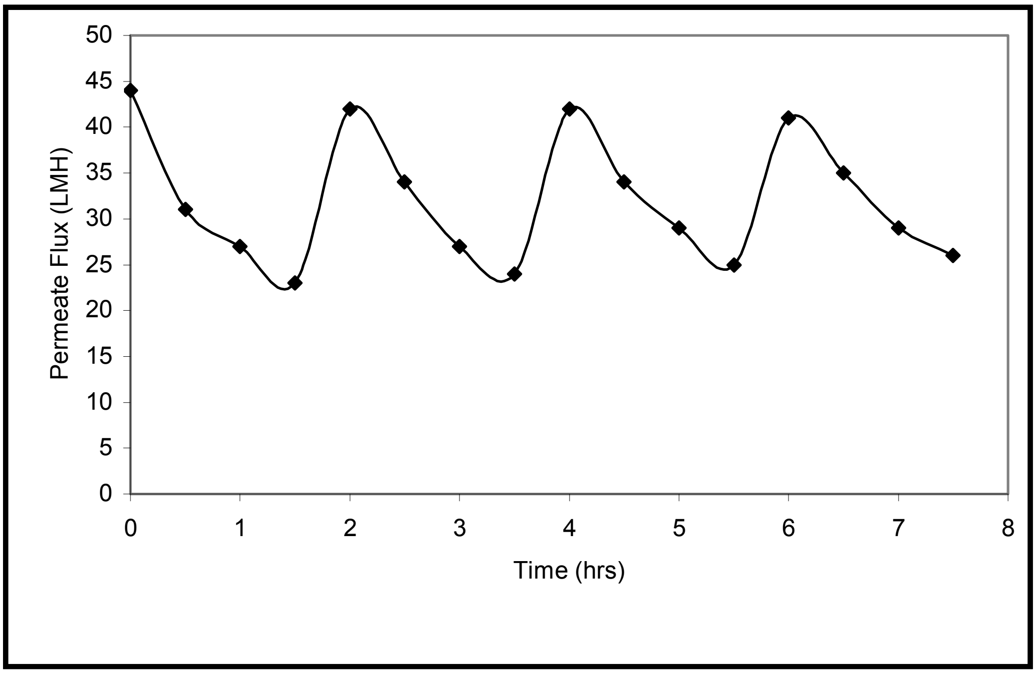


**Figure 7 - Effective backflushing : feed age of 4 weeks**

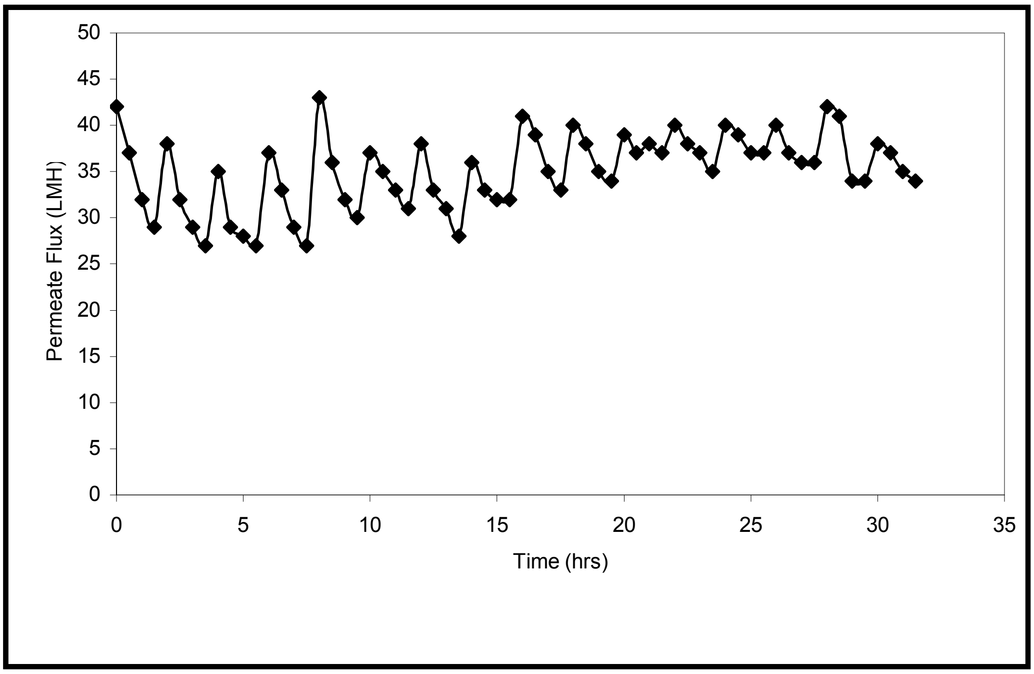


**Figure 8 - Effect of backflushing : feed age of 6 weeks**

Backflushing was very effective in maintaining the permeate flux for all feed ages. The longest run was 33 hours (Figure 8). It is clear that backflushing was very effective in maintaining the flux over this period. The average fluxes obtained at the different feed ages are shown in the table below :

Table 5 : Summary of CUF Fluxes

| **Sludge Age** | **Average flux with backflushing** |
|---|---|
| 3 weeks | 42 LMH |
| 4 weeks | 35 LMH |
| 6 weeks | 35 LMH |

The flux obtained on the 3 week feed seems marginally higher than that obtained with londer feed ages. However, there was no significant difference between fluxes obtained at 4 weeks and 6 weeks feed age.

## 6.2.3. Cleanability

A critical part of performance is whether flux can be recovered after a membrane has been fouled. Three cleaning strategies were investigated to clean fouled membranes :

(i) washing with clean water

(ii) backflushing, i.e. reversing the flow of permeate for a set period

(iii) chemical cleaning. Various mixtures were investigated, and eventually a cocktail of EDTA, sodium laurel sulphate and fresh caustic was selected. EDTA, SLS and NaOH were mixed in equal ratios to give a solution of 0.5% (m/v). This was circulation for 1 hour, whereafter the module thereafter thoroughly washed with water.

<u>Washing</u>

The simplest cleaning technique is to wash out the foulants with clean water. This rarely works in practise, but was investigated for completeness. Figure 9 shows permeate flux profiles obtained using this cleaning technique. Run 1 to Run 4 were conducted sequentially on the same batch of caustic, with clean water washes in between runs.

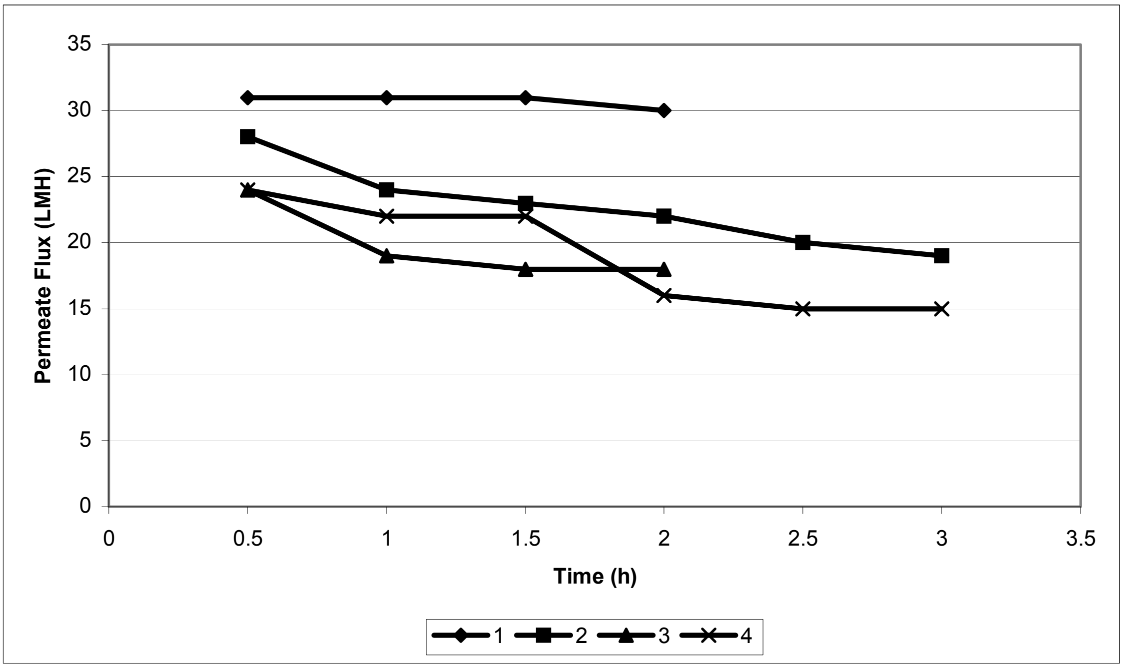


**Figure 9 - Permeate flux profiles obtained using a water wash**

It is clear that washing with clean water has very little potential as a cleaning strategy. The permeate fluxes for each run are lower than previous runs, and there is a progressive decrease from 30 LMH to about 15 LMH.

Backflushing and Chemical Cleaning

The project team subsequently decided to use the membrane's pure water flux (PWF) as an indication of the efficacy of cleaning, rather than permeate fluxes obtained on waste caustic. This would eliminate errors due to differing permeate fluxes amongst different batches of waste caustic.

The procedure in these investigations was as follows :

(i) a new module was made up, and its PWF was measured at a range of pressures.

(ii) The module was then run on waste caustic for a period of three hours. The final flux obtained on the waste caustic was noted.

(iii) The module was then backflushed for approximately 20 minutes. Firstly the feed side was closed off, and clean water was pumped in via the shell side. The clean water permeate the membranes from the outside in, and then left via the reject side of the module. After about 15 minutes, the reject side was closed, and the feed side was opened. After a further 5 minutes, the backflush was stopped, and the module was flushed out by pumping clean water through the membranes, with a negligible transmembrane pressure.

(iv) Following the backflush, the PWF was measured.

(v) The module was then subjected to a chemical clean. The chemical clean was performed using EDTA, SLS and NaOH mixed in equal ratios (m/v). This solution was circulated in the rig for 2 hours. Thereafter the rig was thoroughly washed of traces of the cleaning solution with water.

(vi) The PWF was determined again.

The PWFs so obtained are shown in Figure 10.

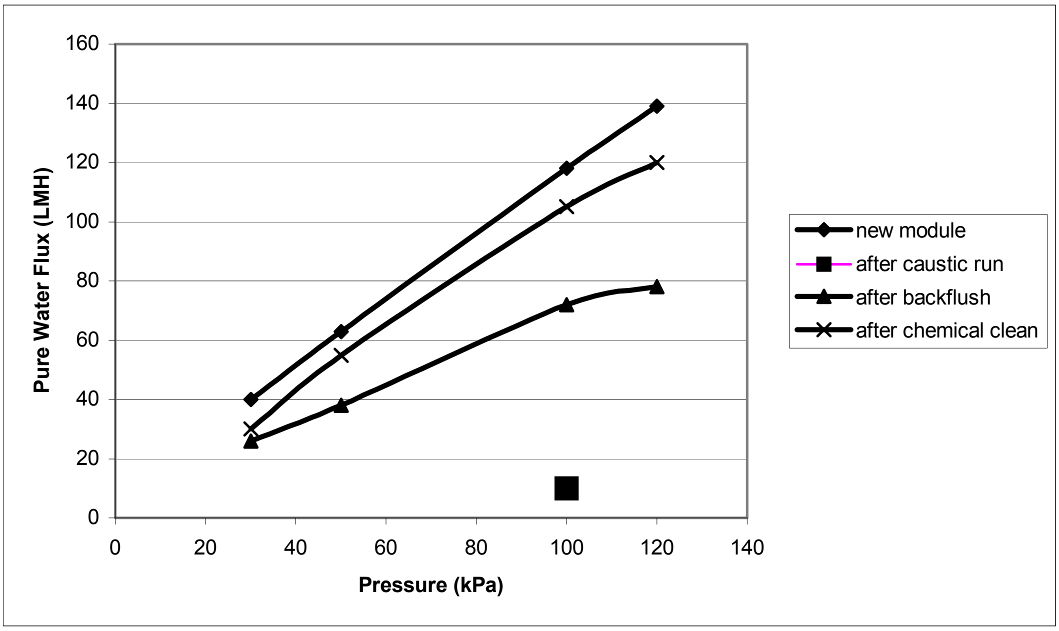


**Figure 10 - Effects of backwashing and chemical cleaning on PWF**

Backflushing restored the PWF to about 60 % of its unfouled value. However, the chemical clean restored the PWP to around 90 % of the initial value. This investigation therefore indicated that the chemical clean was very effective in reversing the fouling of the membrane, and would be a viable method of maintaining membrane permeability.

The efficacy of the chemical clean was then tested on an old, fouled module. The procedure was similar to that above, and the PWFs are shown in Figure 11.

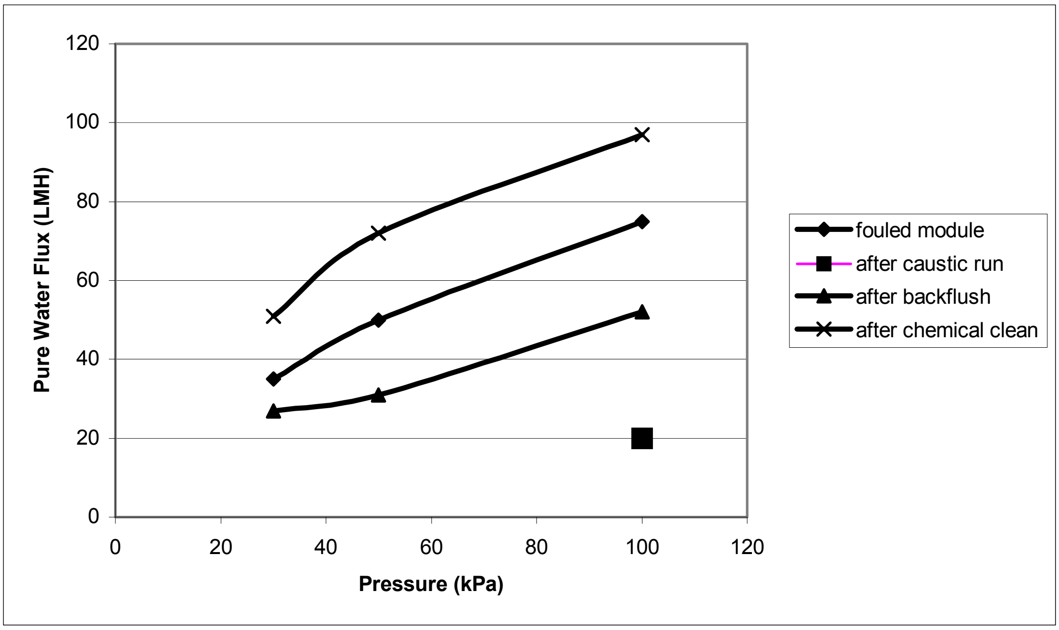


**Figure 11 - Effect of backflushing and chemical clean on an old module**

The fouling on the old module is clearly indicated by the reduced PWF (compare to new module in Figure 10). Once again, backflushing was not very effective in reversing the fouling. However, after the chemical clean, the PWFs were greater than the initial values on the fouled module. This confirmed that the chemical cocktail used was effective in defouling. This investigation also indicated that old fouled membranes could be recovered with the chemical clean.

## 6.3 Summary

In initial trials performed on flat sheet ultrafilters, it emerged that UF was capable of removing between 90 % and 99 % of the suspended solids in the waste caustic. This prompted further detailed investigations into UF using capillary ultrafiltration (CUF) modules based on the #1713 capillary membrane obtained from the University of Stellenbosch. All trials reported here were conducted in a constant concentration mode, i.e. both the permeate (except for samples taken for analysis) and the concentrate were returned to the feed tank.

The turbidity removal was strongly influenced by the feed age, i.e. the period for which the caustic batch had been in use in the bottle washers. At a feed age of 4 weeks, the feed turbidities ranged from 300 NTU to 500 NTU, and the permeate turbidity ranged from 0.7 NTU to 2 NTU. At a feed age of 8 weeks, the feed turbidity ranged from 400 NTU to 500 NTU, while the permeate turbidity ranged from 0.4 NTU to 10 NTU.

Permeate fluxes on a 3 week feed started off at around 50 LMH, and declined to about 20 LMH after 3 hours. However, it was found that backflushing was very effective in maintaining the permeate flux. With backflushing, it was found that permeate fluxes could be maintained at high values for up to 33 hours. Using a backflushing strategy of 5 minutes backflush every 1.5 hours, gave an average flux of 42 LMH for a 3 week feed, declining to an average flux of 35 LMH for a 6 weeks old feed.

Three methods of cleaning the membrane were investigated :- cleaning with water; backflushing; and chemical cleaning. The former two methods were not very effective in restoring fouled membranes. However, it was found that a chemical cleaning using a 0.5 m/v solution of EDTA, SLS and NaOH in equal parts was very effective in removing fouling. With this chemical concoction, fouled membranes were consistently restored to over 90 % of their initial pure water fluxes. Further, it also emerged that old fouled membranes that had been out of use for some time were also restored by the chemical clean.

In overview, CUF emerged as been quite promising for the recovery of waste caustic, with good permeate turbidities, reasonable and stable permeate fluxes, and good cleanability.

# 7 EVALUATION OF TUBULAR NANOFILTRATION

Tubular nanofiltration trials were performed on the ABI caustic at a pressure of 20 bar and a tube velocity of approximately 2 m/s. In between caustic runs, pure water fluxes were determined at different operating pressures.

## 7.1 Turbidity Rejection

The feed turbidities ranged from 250 NTU to 400 NTU. Permeate turbidity profiles are shown in Figure 12. The history of turbidity removal efficiency is shown in Figure 13. Note that in Figure 13, the average permeate turbidity for each run is shown.

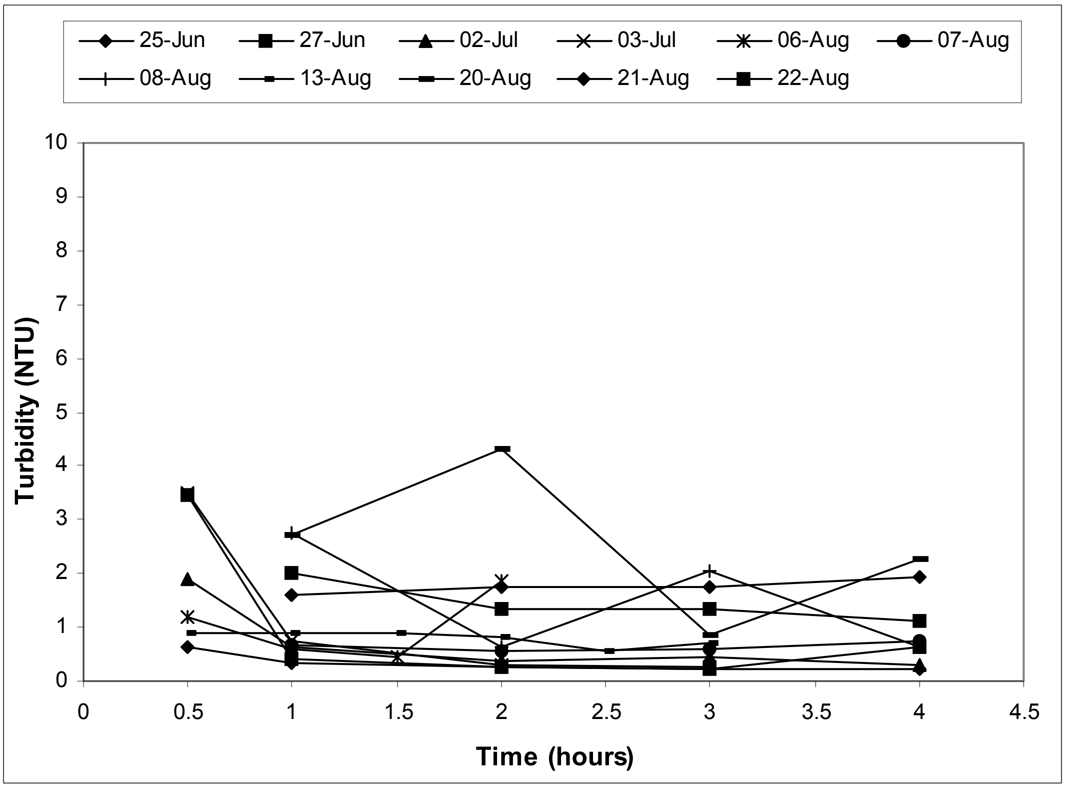


**Figure 12 - Turbidity Rejection : TNF on ABI Caustic**

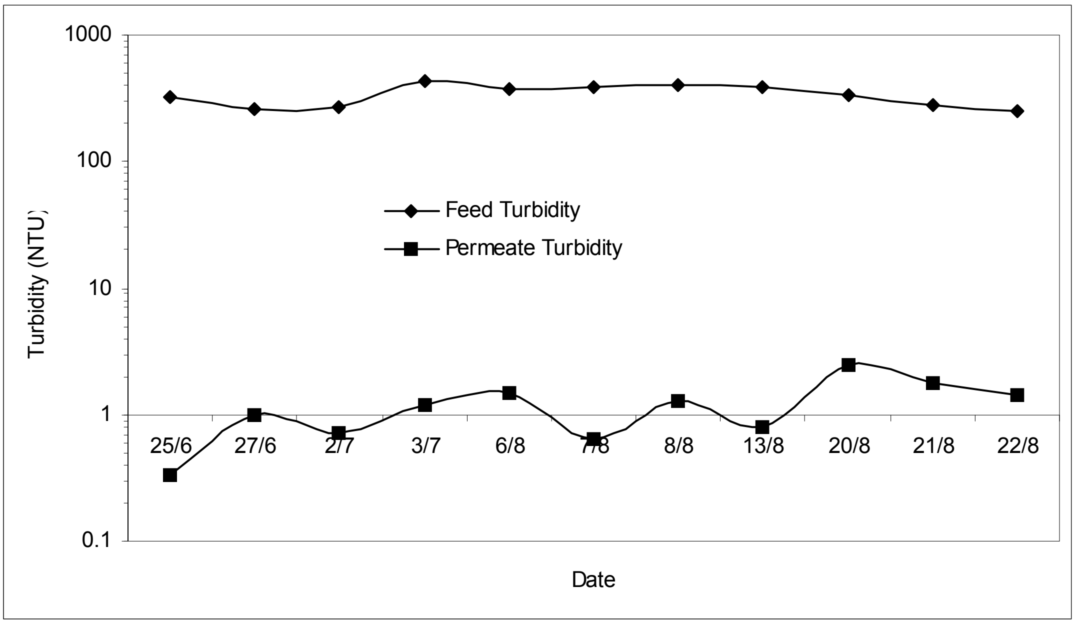


**Figure 13 - History of Turbidity Rejection : TNF on ABI Caustic**

The permeate turbities range from 0.3 to 3 NTU, for feed turbidities of 250 to 400 NTU, indicating an excellent turbidity rejection. However, these turbidities are higher than would be expected of a nanofilter, where turbidities well below 1 NTU should be achieved. There also seems to be a progressive deterioration in permeate quality with time, although there was no similar increase in feed turbidity. This aspect will be discussed further after examination of the pure water and product fluxes.

## 7.2 Permeate Fluxes

Permeate flux profiles obtained on the spent caustic at 20 bar are shown in Figure 14.

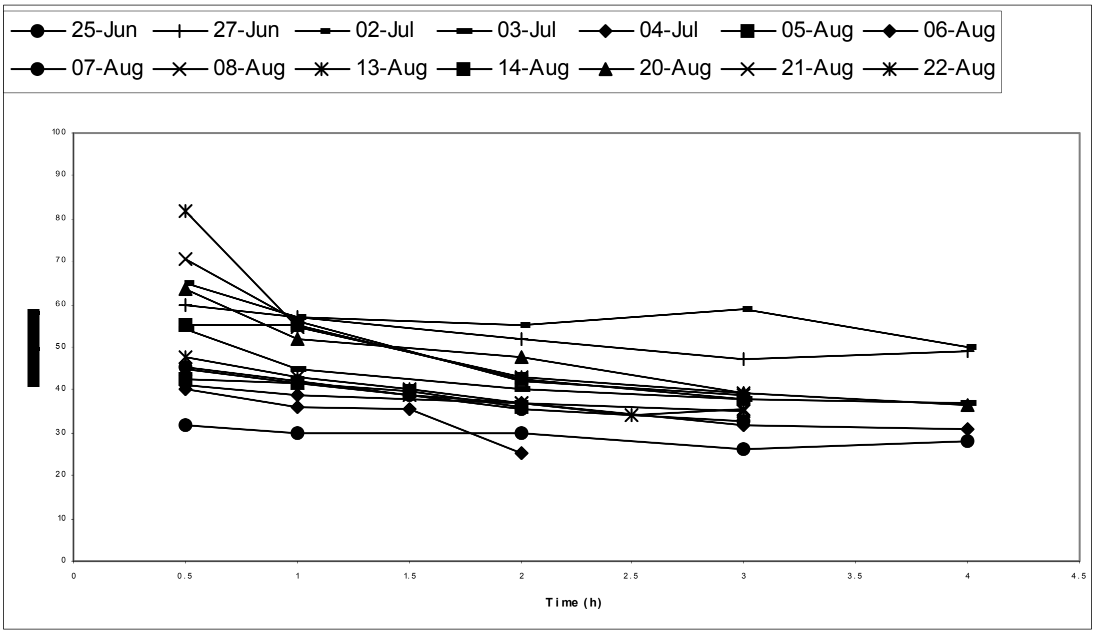


**Figure 14 : Permeate Flux Profiles : TNF on ABI Caustic**

The average flux for each run is summarized in Figure 15.

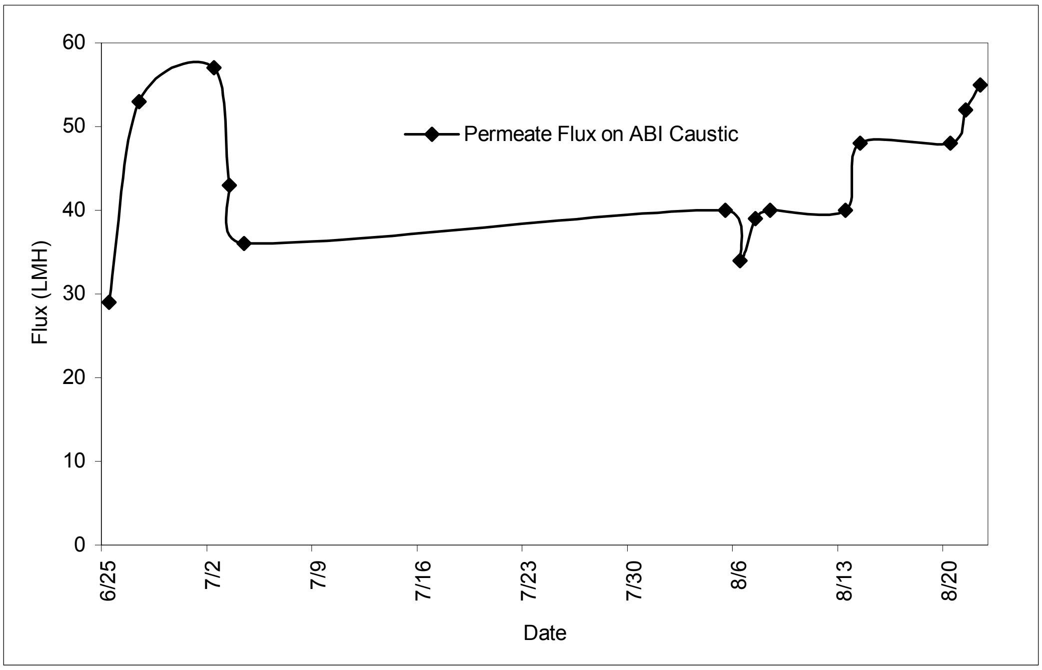


**Figure 15 - Summary of Average Permeate Fluxes : TNF on ABI Caustic**

The product fluxes exhibit a very strange trend. After the first run, there is a significant increase in the flux. This is followed by a rapid decrease, and a further increase.

The pure water fluxes obtained between caustic runs are shown in Figure 16 and Figure 17. Figure 16 indicates the pure water fluxes obtained at different operating pressures, while Figure 17 summarises the fluxes obtained at 20 bar.

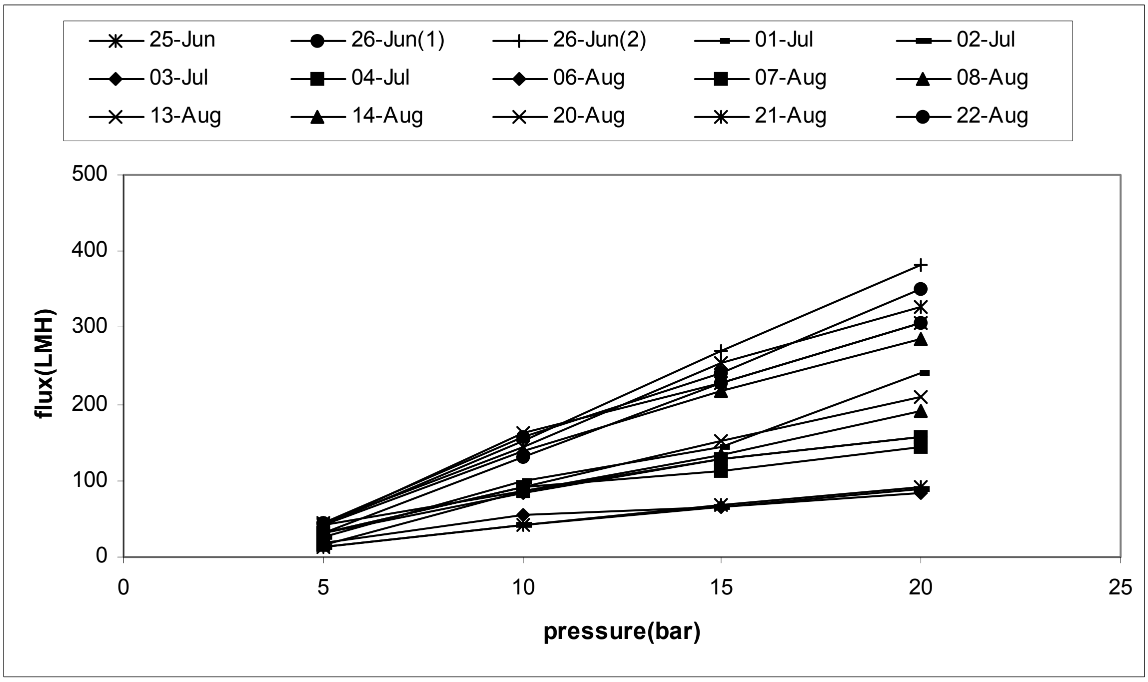


**Figure 16 - Pure Water Fluxes : TNF on ABI Caustic**

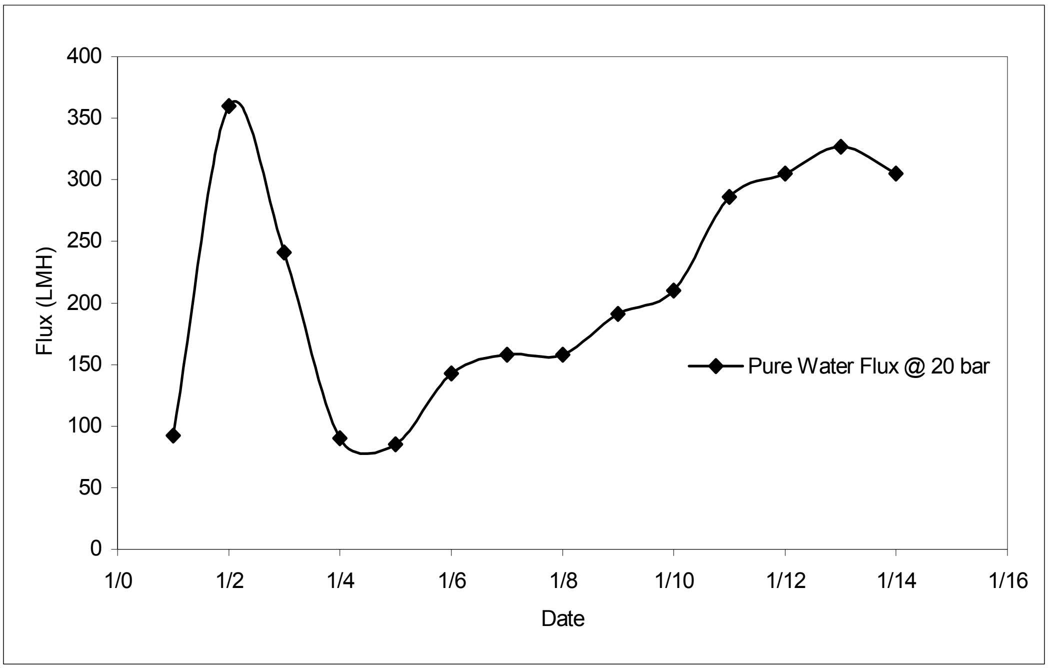


**Figure 17 - Trend of Pure Water Flux at 20 bar : TNF of ABI Caustic**

The pure water flux (PWF) starts of at approximately 100 LMH. It then increases to over 350 LMH, drops back to around 100 LMH, and then slowly increases back to 350 LMH.

The pure water flux at a specified pressure can only increase if there is a change to the structure of the membrane. It is postulated that the following has occurred :

The NF membrane has a thin NF skin on a porous support structure that could be regarded as either an MF or an UF. On exposure to the caustic, or some component in the caustic, some irreversible chemical change occurred in the NF layer, causing the NF skin to slowly degrade. However, the porous support, acting as a MF or UF, retained the suspended solids from the spent caustic. As the NF layer progressively deteriorated further, the membrane became more "open". This caused the permeate flux to increase, and the turbidity rejection to decrease.

Irrespective of whether the above explanation is applicable, the changes in pure water flux indicate that the membrane is most probably changing in response to the caustic, or some component in the waste caustic. In either instance, the TNF membrane tested is not stable when operated on waste caustic.

## 7.3 Summary

The TNF system gives an excellent turbidity rejection, and is capable of cleaning up the spent caustic to the point where it could be reused. However, there are various questions about the stability of the membrane to the spent caustic. In this study, the product flux as well as the pure water flux exhibited very strange behavoirs that possibly indicate a deterioration in the membrane structure.

# 8 COMPARATIVE EVALUATION OF THE DIFFERENT MEMBRANE SYSTEMS

| | Woven Fibre Microfiltration | Capillary Ultrafiltration | Tubular Nanofiltration |
|---|---|---|---|
| **Operating pressure, velocity** | 2 bar, 2 m/s | 1 bar, 1 m/s | 20 bar, 1 m/s |
| **Separation efficiency** | Inconsistent<br>Poor | Consistent<br>Good (product < 10 NTU – 8 weeks old caustic, product < 2 NTU – 4 weeks old caustic) | Consistent<br>V good (product < 2 NTU) |
| **Fluxes** | Not determined due to problems with crossflow system | Average of 35 LMH with backflushing | 30 LMH to 60LMH |
| **Membrane Stability** | Stable | stable | unstable |
| **Cleanability** | Not determined | V good with chemical cleaning | Not determined |

## 8.1 Separation Efficiency

The WFMF gave an inconsistent separation, ranging from poor to very good. This system is unsuitable as a one-step caustic recovery process, but could find an application as a pretreatment step, to reduce the load on a UF or NF membrane system.

Both the CUF and the TNF systems gave a very good to excellent turbidity rejection. The quality of the product is probably adequate for reuse or recycling.

## 8.2 Stability of Membrane

The WFMF membrane is quite stable when operated on caustic, with no obvious signs of degeneration. Hence, it would be suitable for operations on spent caustic.

The CUF membranes also seem to be quite stable on caustic operation, with no indication of performance degradation during the investigations performed here.

The TNF system is unstable, with product and pure water fluxes exhibiting strange trends. It is probable that this membrane is undergoing a chemical change on exposure to caustic.

## 8.3 Economics Aspects

From this study, the two systems that could be considered for caustic cleanup are CUF and TNF, since both give very promising removals of suspended contaminants. The choice of which system should be pursued further will thus depend on the relative economics. A detailed economic evaluation was beyond the scope of this project. However, the relative economics of the membrane systems may be inferred from the availability of membranes (i.e. local or imported), fluxes and operating conditions.

The TNF system gave the best quality of permeate at fluxes ranging from 30 LMH to 60 LMH, at an operating pressure of 20 bar. The CUF system gave a product of slightly lower quality than the TNF, at an average flux of 35 LMH, and operating at 1 bar.

### 8.3.1. Comparative capital costs

The TNF modules are available in areas up to 2.6 $m^2$. The currently available CUF module has a membrane area of approximately 7 $m^2$. The fluxes obtained on TNF are up to 60 LMH, while that obtained on CUF is approximately 35 LMH. Hence, for a specified duty Q (L/h), the number of TNF and CUF modules required are given by :

$$TNF = (Q/60)/2.6 = 0.0064\ Q$$

$$CUF = (Q/35)/7 = 0.0041\ Q$$

It is seen that for a given duty, the number of TNF modules required would be about 1.5 times the number of CUF modules required.

The TNF system would have to constructed of stainless steel, due to the high operating pressure. The CUF system is constructed of PVC, available locally.

Hence, even without detailed prices being available, it is clear that the capital cost of a TNF system would be greater than that of a CUF system, for a specified duty.

#### 8.3.2. Comparative energy costs

The operating pressure for the TNF system is 20 times that of the CUF system. Hence, the energy requirements would be of a similar magnitude. There is not expected to be any significant difference in operator requirements, since both systems could be designed to be manually operated or fully automated. Hence, the operating cost for the CUF system is expected to be substantially lower than that of the TNF system.

#### 8.3.3. Maintenance and module replacement

There is not expected to be a significant difference in maintenance of a TNF and CUF system. The replacement of membranes for the CUF system is expected to be less than the TNF system, in view of the fact that they are imported, and in view of the poor prevailing exchange rates.

#### 8.3.4. Summary

In summary, both the capital and operating costs of the CUF are likely to be lower than that of the TNF system. In view of the fact that the separation efficiency of the TNF system is only marginally better than the CUF, it may be concluded that the CUF would be more economically attractive for caustic cleanup.

## 9 CONCLUSION

WFMF gave a very inconsistent product quality, ranging from poor to very good. The system would not be suitable to clean up used caustic for reuse. In larger scale applications, however, it may be preferable to use WFMF to pretreat the waste caustic, prior to cleanup by CUF or NF.

CUF gave a very good product quality, from 1 NTU to 10 NTU, probably suitable for direct reuse. Average fluxes range from 35 LMH to 42 LMH, and could be maintained for up to 32 hours with regular backflushing. The membrane was stable to caustic, and fouled membranes could be recovered with chemical cleaning.

TNF gave an excellent product quality, generally around 1 NTU. However, the permeate fluxes and pure water fluxes were inconsistent and changed drastically with time. This is most probably indicative of a change in membrane structure, indicating possible instability when operated on waste caustic.

In considering economic aspects, the capital cost of a CUF system is likely to be significantly lower than a TNF system. The operating costs of the CUF system are also likely to be lower, due to lower operating pressures. Maintenance costs may not differ musch between CUF and TNF. Overall, therefore, the CUF system is likely to be more cost effective than a TNF system, while the TNF produces a higher quality of product.

# 10 RECOMMENDATIONS

The following aspects need to be addressed further in order to progress to the industrialisation of a local membrane system for caustic reuse :

(i) Criteria for reuse of caustic – The project team were unsuccessful in obtaining from the beverage bottlers a clear indication of the criteria that recycled caustic must meet to be considered for reuse, seemingly because caustic reuse had not been given serious consideration previously. The caustic suppliers should have a better understanding of the criteria that caustic cleaning solutions must meet, but were reticent in revealing this information.

(ii) Economic evaluation – Ultimately, the cost of recycling caustic must be compared to the cost of using fresh caustic. This requires information on criteria for reuse, additives in the caustic solution, and the cost of fresh caustic and additives. Once again, this information could not be obtained from the bottlers.

(iii) Performance in batch concentration mode – The permeate fluxes obtained in this study were obtained by operating in a constant concentration mode. This will simulate the situation where a side stream is continuously drawn off from the bottle wash bath and cleaned. Alternatively, the caustic cleanup could be done in a batch concentration mode. Design fluxes for this mode cannot be inferred from this study, but can easily be obtained experimentally.