Membrane performance restoration. I: Abattoir process streams, cleaning regimes for UF membranes

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Abstract

Ultrafiltration offers attractive advantages in the treatment of effluent streams originating from an abattoir. However, severe fouling caused by the presence of proteinaceous and fatty constituents in such streams reduce membrane transport rates to unacceptable levels in a very short period. Cleaning regimes by which membrane transport rates can be restored and maintained effectively have been evaluated both in the laboratory and applied in the field with success.

Introduction

Most commercial ultrafiltration (UF) membranes are manufactured from hydrophobic polymer materials as these materials are chemically, physically and mechanically more robust than their hydrophilic counterparts. Although the chemical resistance and mechanical properties of these membranes allow them to be used under sometimes harsh and hostile conditions, their hydrophobic properties can often be the cause of drastic loss of flux due to fouling.

As a unit operation of separation, UF offers some attractive advantages with respect to reducing the chemical oxygen demand (90%) and phosphate loads (85%) of wash and process water effluent streams that originate from abattoirs (Cowan et al., 1991). However, these streams contain numerous proteinaceous, fatty and other constituents, and when such an effluent is treated by UF membranes, fouling of the membranes and a loss of product flux are inevitable (Binnie and Partners, 1988a; 1988b).

Certain pretreatment steps such as screening and air flotation to remove fat and other bulky materials are a minimum requirement in such a strategy, as these operations reduce the solids load in the feed and the rate of fouling to some extent. However, fats and proteins readily pass these initial pretreatment operations, so that their potential to foul membranes remains unchanged (Hartmann, 1991).

It is therefore unwise to operate hydrophobic polysulphone or poly(ether sulphone) UF membranes on abattoir effluent streams without the use of some strategy by which the original pure-water flux of the membranes can be secured.

Animal fats (lipids) are one constituent of an abattoir effluent which can cause severe fouling of hydrophobic UF membranes. Fats give rise to particular problems because of their low solubility in water and their hydrophobic nature (membrane adsorption potential).

Proteins, another major constituent in the effluent stream are macromolecular substances that are fibrous or globular in shape, but completely looses this conformation when denatured. They consist mostly or sometimes entirely of polypeptide molecules which are co-polymers of sets of 20 different α-amino acids which may have polar or non-polar residues or ionisable groups.

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Proteins that contain many charged groups can, for example, be precipitated by changing the ionic strength or organic solvent content of the solution. Precipitation of protein and/or adsorption of substances (Lips and Jessup, 1979) greatly affects the performance of a membrane (Ostrovskii et al., 1990).

The only non-specific method that will ensure total solubilisation and subsequent removal of proteinaceous precipitates, for example, is to degrade the protein into smaller peptides or amino acid monomers. The peptide bond in all proteins is quite stable, and complete hydrolysis of all these bonds in nature is accomplished with the aid of a group of very specialised molecules called proteases or proteolytic enzymes. These proteinous catalysts specifically break the peptide bonds to yield shorter peptides and ultimately amino acid monomers.

This paper describes a different approach to securing effective cleaning agents for UF membranes operating on an abattoir process effluent. In this study, industrial materials, proved by the abattoir industry to be effective cleaning and sanitising agents, were evaluated first in the laboratory and then in the field for their ability to restore the pure-water flux (PWF) productivity of UF membranes. Also of importance was to determine to what extent these materials might be harmful to the membranes.

Experimental

Materials

Ultrafiltration membranes

In the laboratory studies, a 2,4 m module with 719-series 13 mm diameter tubular poly(ether sulphone) UF membranes, that had been operating in a pilot plant on effluent from the Cato Ridge Abattoir in Natal, was obtained through Membratek. The module had been operated under adverse conditions and the membranes were severely fouled.

Cleaning agents

The experiments that were conducted to determine the effectiveness of cleaning materials, centered on the use of 2 commercial products, one a proteolytic enzyme-based formulation (used in conjunction with sequestering, wetting and emulsifying agents, all specially formulated for use in the abattoir industry), and the other a mild chloralkali sanitiser.

TABLE 1
CLEANING AGENTS FOR SOILED ABATTOIR-OPERATED UF MEMBRANES

Cleaner	Comments	Concentration	Components
Enzyme-based detergent	Used in 1:1 ratio with synergiser	1 to 3%	Stabilised enzymes Non/anionic wetting agents Emulsifiers
Synergiser		1 to 3%	Mild alkalis Sequesterants Water softeners pH 10,2 buffered
Chloralkali	Steriliser (peptiser)	1 g/ℓ	mild chlorinated alkali pH 10,7 buffered

TABLE 2
DIFFERENT *IN SITU* CLEANING REGIMES FOR MEMBRANE FLUX RESTORATION

Treatment	Description
I	3% proteolytic enzyme rinse
II	1% proteolytic enzyme rinse
III	1 g/ℓ chloralkali rinse
IV	50°C hot-water flush/rinse/flush
V	4 x foamball/air swabbing
VI	21°C tap-water flush

Table 1 gives information on the cleaning agents that were used, and their recommended concentration levels. Table 2 summarises the different cleaning regimes that were tested during the laboratory and subsequent field evaluations.

Cleaning sequences

Soak rinse (laboratory)

Soak rinse tests were performed in glass beakers at 25°C by allowing short sections (100 mm) of the soiled membranes to soak in the cleaning agents for long periods. The soak studies were performed with very gentle stirring, and the cleaning agents were regularly replaced with fresh solutions.

Manual rinse (laboratory)

Manual rinse tests were performed on longer membrane sections (500 mm), by loading a membrane into a test cell half-filled with a particular cleaning agent, and shaking the cell for 10 min.

Dynamic rinse

In the dynamic rinses performed in the laboratory, test cells containing the membranes were placed in a test loop (4 x 500 mm-long membranes connected in series), and all the rinses and evaluations were performed *in situ* without disturbing the membranes after they had been loaded. A 5 ℓ vessel was used as a feed tank for the cleaning solutions which were circulated through the cells by means of a centrifugal pump (linear velocity 2,5 m/s, inlet pressure 100 kPa). The 5 ℓ tank was not equipped with a cooling coil, and the temperature increased steadily from an ambient 20°C at a rate of 1,0°C/min during a chemical rinse cycle.

The pilot plant was equipped with a 200 ℓ clean-in-place (CIP) tank fitted with a steam heater which allowed preheating of cleaning solutions. At the start of a cleaning operation the process fluid inside the modules was first flushed from the system with the cleaning solution, before the solution was recirculated back to the CIP tank.

Foamball swabbing

Four foamballs were inserted manually into test cell (laboratory) or module inlets (pilot plant) when a foamball rinse cycle was required. The water which drained from the membranes was not replaced, to allow air into the membrane tubes on purpose. As with all other rinse cycles, the back-pressure valve remained fully open for this cycle, which resulted in a very effective combination foam ball/air scour.

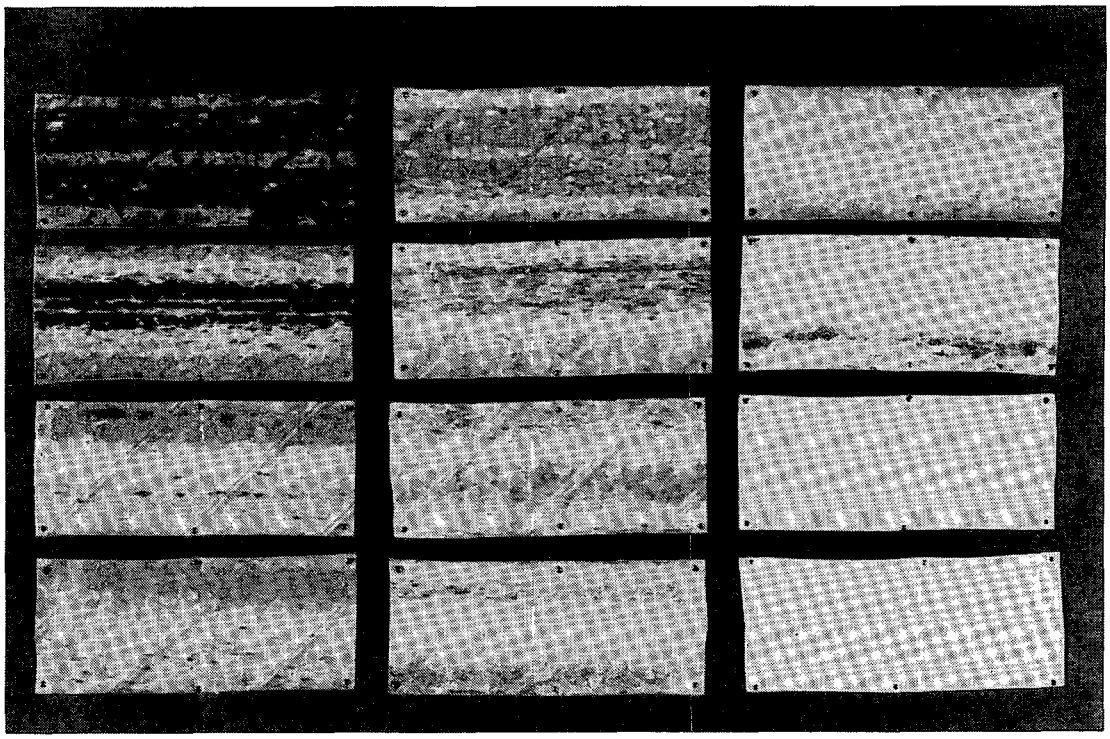
Cleaning performance evaluation

The PWF versus operating-pressure relationships of the membranes were used to compare performances before and after cleaning operations.

In the laboratory the linear-flow velocity was kept at 0,5 m/s to maintain low pressure drops across the test-loop during PWF tests. The temperature in the PWF test-loop was maintained at 20 ± 0,1 °C.

The laboratory investigations on cleaning chemicals were repeated in the field, where the end-of-the-day PWF of UF modules operating on process water from the Cato Ridge Abattoir also served as the basis for comparing the effectiveness of the different cleaning regimes.

The abattoir worked a single day-shift and the UF plant was operated only during this time. Cleaning was performed before shut-down in the afternoon or before start-up in the mornings, and the UF plant was operated on effluent for an average of 6 h/d. The PWFs were routinely monitored before and after cleaning.



Fouled membrane	48h	159h
Fouled membrane	112h	167h
24h	118h	183h
41h	135h	Unused membrane

Figure 1
Photograph of sections of tubular membranes subjected to a proteolytic enzyme/synergiser cleaning solution

Results and discussion

Laboratory study

Inspection of the fouled membranes received revealed that the membrane surfaces were coated with a brown apple-peel-like deposit, thick in some places. As can be seen in the photograph (Fig.1), the heavy deposit was not evenly distributed over the membranes, and the fouling was noticeably more severe in certain areas than in others.

Differential scanning calorimetry (DSC) analysis was performed on scrapings of the deposits on the membrane to obtain some understanding of its nature. The DSC thermograph (Fig. 2) shows a broad melting peak in the temperature range 25 to 70°C with a peak melting point of ~50°C. This type of peak is characteristic of low molecular-mass substances such as waxes and fats. It therefore suggested that some of the fouling material adhering to the membrane contained some form of animal fat.

The PWF of the fouled membranes showed large standard deviations due to the foulants present on the membrane surface (See Fig. 3). For this reason the membranes were compared rather on the basis of their normalised fluxes, i.e., the PWF of the fouled membrane was taken as unity.

In a static test, performed with a 3% solution of the proteolytic enzyme and synergiser, it was noticeable how the foulant layers swelled and in places became dislodged from the membranes under the gentle stirring action. The highly swollen deposit could be scraped easily from the surface, which was not possible with

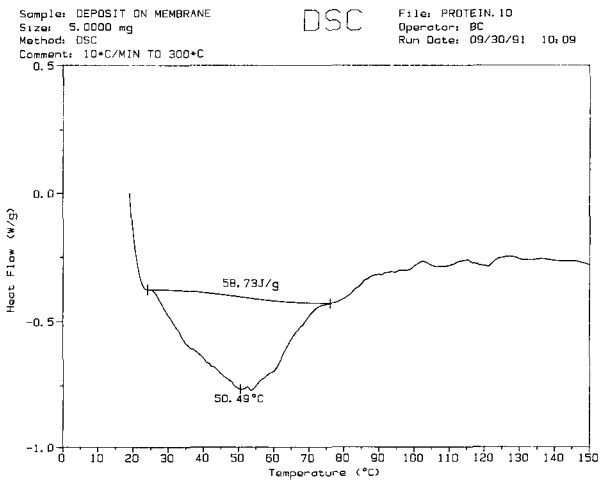


Figure 2
DSC analysis performed on the scraping from a fouled membrane

membranes which had not undergone the enzyme treatment. The surfaces of the membranes shown in Fig. 1 were never touched. It is clear from these results, however, that the enzyme preparation is at least capable of dislodging protein and other precipitates from the membranes (The cumulative contact time of

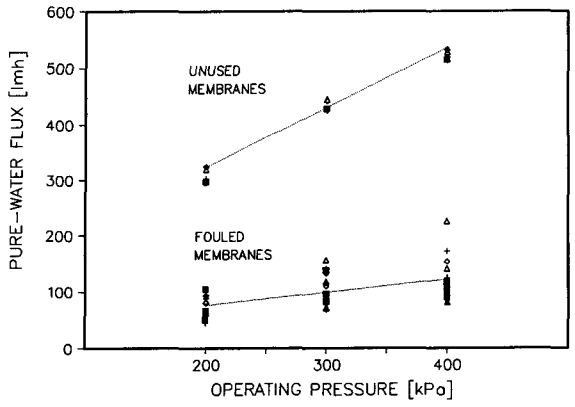


Figure 3
Baseline pure-water flux (PWF) of fouled versus unused membranes

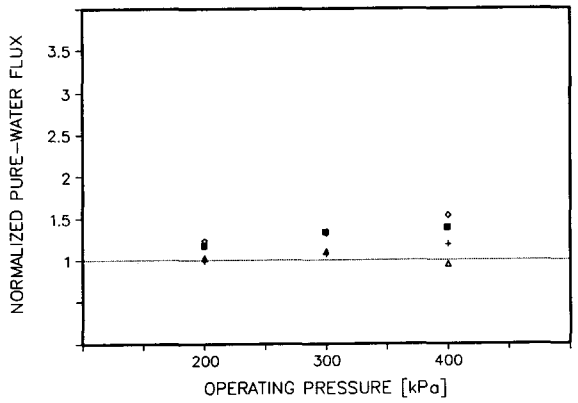


Figure 4
Effect of cleaning regime I (manual, 10 min, 21°C rinse) on normalised PWF

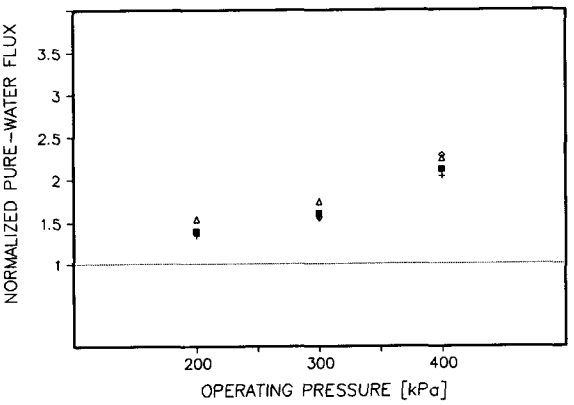


Figure 5
Effect of cleaning regime I and V (dynamic, 30 min, 21 to 50°C) on normalised PWF

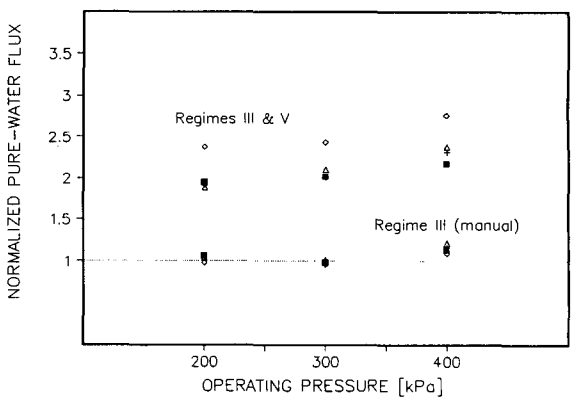


Figure 6
Effect of cleaning regime III (manual, 30 min) and cleaning regimes III and V (dynamic, 20 min, 21 to 40°C) on normalised PWF

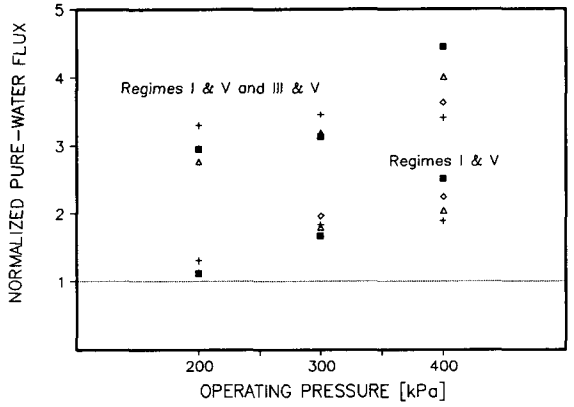


Figure 7
Effect of dynamic cleaning regimes I and V (30 min, 21 to 50°C) and cleaning regimes I and V (30 min, 21 to 50°C) followed by cleaning regimes III and V (10 min, 21 to 30°C) on normalised PWF

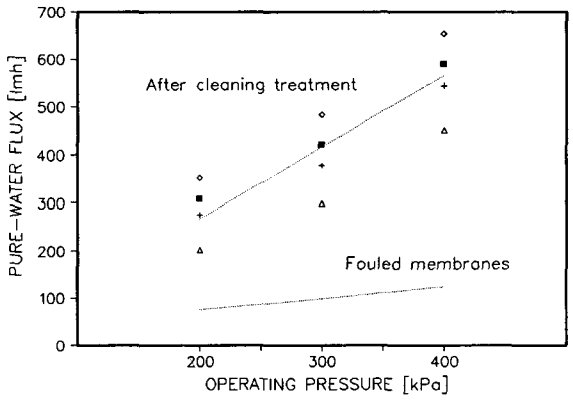


Figure 8
PWF comparison between fouled membranes and membranes treated with cleaning regimes I and V (30 min, 21 to 50°C) followed by cleaning regimes III and V (10 min, 21 to 30°C)

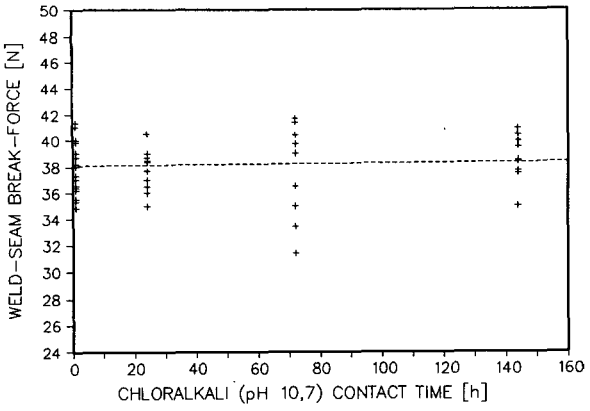


Figure 9
Effect of the chloralkali cleaner on the tensile properties of the weldseam

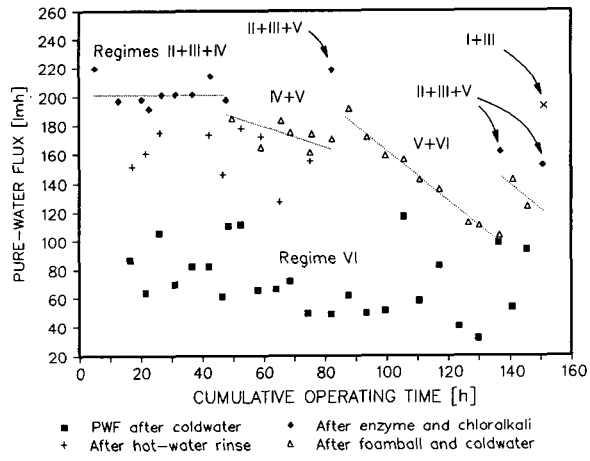


Figure 10
Effect of different cleaning regimes on PWF performance of UF pilot plant

the different membranes with the enzyme active cleaner is given in the key below the figure).

No evidence of embrittlement or of other loss of membrane integrity was noticed after the membrane samples had been in contact with the 3% enzymatic/synergiser cleaner for 183 h.

Figure 4 shows the effect of a 10-min manual rinse with a 3% enzyme/synergiser solution on the PWF performances of the fouled membranes.

In comparison, the cleaning operations conducted in the dynamic mode, in which the temperature rose to 50°C due to recirculation, had a more pronounced effect on improving the PWF performance of the membranes than did the manual rinse at ambient temperature. Figure 5 shows a nearly twofold increase in the PWF obtained with a dynamic 30-min enzyme/synergiser treatment, in combination with the foamball/air scour, at the higher temperature (Regimes I + V).

The same improvement resulted when membranes were treated with the chloralkali peptising solution (Regime III). At the recommended concentration of 1 g/ℓ, this solution contained ~ 150 mg/ℓ free chlorine.

The results of a 10-min manual chloralkali rinse (21°C) performed on one set of membranes are shown in Fig. 6. The figure also shows the results of a 20-min dynamic rinse, in combination with a foamball/air scour (Regimes III + V), performed on another set of membranes (rate of temperature increase ~ 1,0°C/min). A significant improvement, with the PWF more than doubling, was observed.

In Fig. 7 the results of combination treatments are compared. Here the membranes were first subjected to a 30-min enzyme/synergiser and foamball rinse (Regimes I + V). The PWF was determined, and the membranes were subsequently subjected to a 10-min chloralkali rinse, followed by a foamball/air rinse (Regimes III + V). These treatment combinations brought about a threefold increase in the PWF of the membranes and restored the pure-water transport rate to within 5% of its original value.

The summary shown in Fig. 8 reveals the extent to which flux restoration was possible in the laboratory study. Upon removal of the cleaned membranes, and on closer inspection of the internal and external surfaces of the membrane tube, the membranes themselves were shiny and appeared clean, although the substrate still had a slightly yellow tint.

A large number of membranes were also soaked in the chloralkali solution to determine whether extended contact with this cleaner would, at the recommended concentration of 1 g/ℓ, have any detrimental effect on the mechanical integrity of the weldseam of the polyester substrate material (The stoppered soak-bath was maintained at 24°C and refreshed daily). Figure 9 shows that although there appears to be a large scatter in the strength of the weldseam, no deterioration in the tensile properties was evident over the period tested.

Field study

Figure 10 shows the results of the first 150 h of pilot-plant operation during which the effects of various cleaning regimes were evaluated. At the end of each day the pilot plant was flushed with 21°C tap water before the end-of-day PWF values were measured and any cleaning initiated.

It is evident from the results presented in Fig. 10 that daily enzyme, chloralkali and hot-water rinses (Regimes II + III + IV), maintained PWF values of the membrane modules at their average starting values .

A steady decline in the PWF was noticeable when the enzyme and chloralkali regimes were replaced by hot water (50°C) and foamball rinses only (Regimes IV + V). This decline was temporarily halted at 84 h of operation when a single enzyme, chloralkali treatment and foamball rinse were conducted (Regimes II + III + V), which restored the PWF to its original value.

However, when the operation was continued with foamball swabbing and tap-water rinses as the only cleaning regimes employed (Regimes V + VI), the decline in PWF was even more evident as happened with the hot-water and foamball rinses (Regimes IV + V).

After the PWF had been allowed to decline to very low values, a cleaning regime, comprising a 30-min rinse with enzyme active agents, a 10-min rinse with the chloralkali and a foamball swabbing (Regimes II + III + V), was brought into effect. This cleaning operation yielded a good improvement in the PWF. However, the effort was not totally successful, and the previous treatment was repeated with a 3% concentration level 30-min rinse of enzyme/synergiser (Regime I) as opposed to the 1% of

Regime II. This treatment restored the PWF to the original value, as can be seen in Fig. 10.

Conclusions

The laboratory study conducted on UF membranes obtained from the pilot plant at Cato Ridge Abattoir revealed:

- Indications that lipids (fats) are probably present on the surface of the membranes.
- Low-temperature rinsing (21°C) with cleaning solutions is not as effective as medium-temperature (50°C) operations (The average melting-point of the fatty deposits on the membrane surface appears to be ~ 51°C).
- Foamballs are very effective in removing the loosened deposits by a scouring action; particularly if air is introduced simultaneously to increase turbulence.
- Proteolytic enzyme cleaners, especially those which have been developed and designed for use in the abattoir industry, are effective in breaking up the foulant deposits on a poly(ether sulphone) UF membrane.
- Membrane flux restoration is improved when a proteolytic enzyme-cleaner rinse is followed by a chloralkali rinse (NB: 10-min rinses, conducted at 40 to 50°C, followed by foamball cleaning, proved extremely effective when conducted immediately after the enzyme wash).
- The chloralkali solution used has a buffered pH of 10,9* with a ~ 150 mg/ℓ concentration if used at the recommended concentration level of 1 g/ℓ. The chloralkali did not have a detrimental effect on the weldseam strength over a test period of 164 h (*Note: The pH level of commercial cleaners can be high (>pH 11) and it is always recommended that the membrane supplier be consulted first before unprescribed materials are used).
- Laboratory evaluation of cleaning regimes and materials can supply valuable information when pilot-plant operations are under evaluation.

Acknowledgements

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