

# THE RECOVERY OF BRINE FROM RESIN REGENERATION EFFLUENT BY NANOFILTRATION

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## Abstract

The recovery of brine from the effluent obtained by the regeneration of ion exchange resin at Hulett's Refineries has been investigated on a pilot plant scale, using nanofiltration, a pressure-driven membrane filtration process. The technology proved suitable, with a sodium chloride permeation of 96% and organic colour removal (as total carbon) of 81%, yielding recovered brine of a quality acceptable for re-use. Results indicate a potential saving in sodium chloride usage of 60% and a reduction in effluent disposal costs of 30%, limited mainly by water balance constraints.

## Introduction

At Hulett's Refineries colourants are removed from the sugar liquor using special anion exchange resins. Desorption of the colourants from the loaded resin is achieved using an alkaline sodium chloride solution. The regeneration waste poses a disposal problem due to its high salinity and Biological Oxygen Demand (BOD). Reclamation of brine from the waste regenerant stream would reduce the volume of effluent to be disposed and would reduce the quantity of fresh salt required to make up the regenerant solutions. A method of brine recovery involving nanofiltration, a pressure-driven membrane process, has been investigated.

## Decolourisation and regeneration processes

The raw sugar solution is decolourised first by carbonation and then by passing the liquor through an acrylic strong base anion exchange resin. The resin process involves the adsorption of the colourants in the sugar liquor onto the resin. The process is two-stage, taking place in five parallel trains of two vessels each, each vessel containing 16 m<sup>3</sup> of resin. The sugar liquor is heated to 84°C to reduce its viscosity, and is passed through the row of vessels containing older resin and then through the row containing the newer resin. The service cycle of the resin is 24 hours.

Desorption of the colourants is achieved by regeneration of the resin, which is carried out using an alkaline (pH 12) brine containing about 110 kg/m<sup>3</sup> of sodium chloride, at 84°C. One pair of resin vessels is regenerated at a time, with regenerant being passed first through the newer resin, then through the older resin. Part of the effluent is recycled for re-use in the next regeneration.

The resin undergoes an acid wash every 20 cycles using a solution containing about 40 kg/m<sup>3</sup> of hydrochloric acid. This removes inorganic precipitates and some polymeric organic structures. The acid is displaced with recycled brine and the resin is neutralised with an alkaline solution. Thereafter, regeneration with fresh brine is performed. The overall effluent from the acid wash is acidic and must be neutralised with lime before discharge. This effluent, plus the regeneration effluent that is not recycled, is transported by road tanker to disposal via deep sea outfall.

## Nature of the regeneration waste

The regeneration waste (excluding the acid wash effluent) contains mostly sodium chloride (up to 110 kg/m<sup>3</sup>) and organic matter (up to 6 kg/m<sup>3</sup> as total carbon), has a pH of 8 to 9 and contains negligible suspended solids. It constitutes approximately 65 m<sup>3</sup> per regeneration, or 260 m<sup>3</sup> per day. Table 1 summarises available information on the nature of the organic colourants (Getaz, 1988; Schoute-Vannek, personal communication).

Table 1  
Constituents of the Effluent

Compound	Molecular mass (g/mol)	Charge (-ve)	Colour at pH 9
Natural (cane juice):			
Phenolic acids	< 10 000	yes	low
Flavonoids	< 10 000	yes	high
Sugars	< 1 000	no	none
Factory produced:			
Reaction products of phenolic acids	10 000 to 25 000	no	high
Alkaline degradation products of reducing sugars	10 000 to 25 000	no	high
Caramels	> 25 000	slight	high
Melanoidins	> 25 000	slight	high

In order to characterise the regeneration effluent, samples of the effluent were taken at 5 minute intervals during a regeneration cycle and analysed for chloride and total carbon concentrations. That portion of the regeneration stream which was directly recycled was not sampled. Figure 1 shows a typical concentration profile.

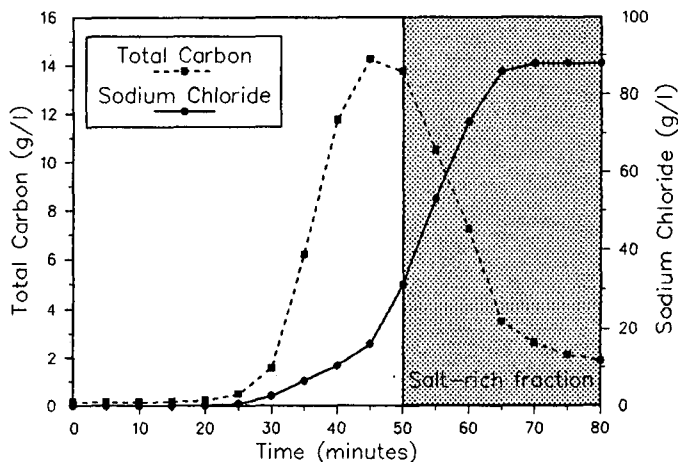


FIGURE 1 A typical concentration/time profile for the regenerant effluent.

The initial fraction of the effluent is low in sodium chloride, but contains a large proportion of the organic matter. Attempts to recover all the effluent would result in the production of excess low concentration brine. Attention was therefore focused on the latter fraction, with a 50-minute cut-off point chosen on the basis of water balance considerations. The fraction between 50 and 80 minutes will be referred to as the "salt-rich" fraction, and includes 86% of the sodium chloride, while excluding 63% of the organic matter (as total carbon) present in the effluent.

### Previous work

Several processes for the recovery of brine from resin regeneration effluent have been tested. The merits of each of these have been summarised by Meadows *et al.* (1992).

Wadley and Buckley (1991) carried out laboratory tests on the Hulett Refineries resin regeneration effluent employing nanofiltration. They used 0,6 m lengths of 12,5 mm diameter tubular samples of SelRO™ MPT-10 and MPT-30 membranes. In a typical experiment, a feed containing 74 kg/m<sup>3</sup> of sodium chloride and 3 kg/m<sup>3</sup> of total organic carbon was batch concentrated to 70% water recovery. The total organic carbon removal was 95% and 91% and the sodium chloride recovery was 61% and 63%, for MPT-10 and MPT-30, respectively.

### Proposed process: nanofiltration

Nanofiltration, also known as charged membrane ultrafiltration or selective reverse osmosis, is a pressure-driven membrane filtration process. The membrane consists of a hydrophobic ultrafiltration substrate with a high density of negatively charged hydrophilic groups bonded onto the surface. The negative surface charge causes repulsion of anions, leading to a decrease in solute passage with increasing valency of the anion. However, salt passage increases with increasing valence of the cation due to membrane charge shielding. High electrolyte concentrations also cause shielding, thus reducing the selectivity of the membrane and increasing solute passage (Mickley, 1985).

Monovalent ions of low charge density readily permeate the membrane, while large molecules and highly charged molecules have very low permeation rates. The nominal molar mass cut-off for many commercially available nanofiltration membranes is 400 g/mol.

Figure 2 is a schematic representation of the nanofiltration process in a single tube. The part of the solvent and solute that diffuses through the membrane is referred to as the permeate, while the remaining solution is called the retentate. The aim of applying nanofiltration to the resin regeneration effluent is to recover the purified brine in the permeate and to concentrate the organic matter in the retentate.

This effluent is suited to treatment by nanofiltration since the organic matter present is predominantly of high molar mass or is negatively charged or both. The retention of NaCl is low even in pure solutions, but the presence of charged organic matter can enhance its passage further (Perry and Linder, 1989).

Nanofiltration was chosen in preference to ultrafiltration as it offers significantly higher removal of organic matter and higher resistance to fouling. Low molar mass organic matter (less than 1 000 g/mol) is not usually retained by ultrafiltration membranes. The accumulation of such compounds in the recycled brine may have an adverse effect on resin regeneration.

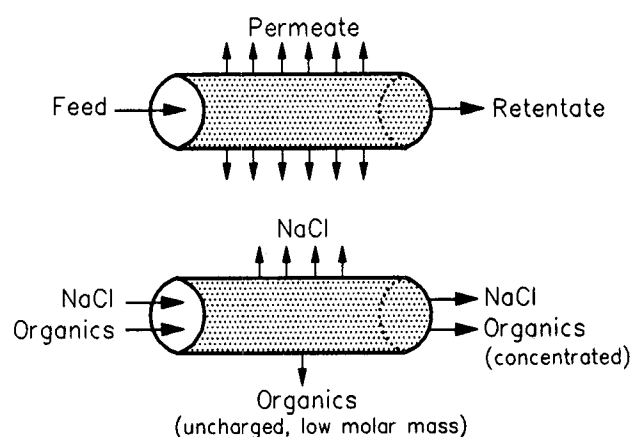


FIGURE 2 Schematic diagram of the nanofiltration process applied to brine recovery

### Membrane selection

Since the regeneration process is carried out at 84°C, it would be advantageous to operate the brine recovery process at a high temperature. Hence a membrane with high thermal stability is required. The pH of the regeneration effluent is usually 8 to 9, which is tolerated by most commercially available nanofiltration membranes.

The membranes are available in tubular or spirally wound configurations, of which the latter is cheaper. However, the spirally wound membranes must be operated at relatively low temperatures (usually less than 45°C). For viscous fluids, higher cross-flow velocities are attainable through the tubular elements, reducing the build-up of surface gel layers. The use of tubular elements also eliminates the possibility of clogging of the system by particulates. The SelRO™ MPT-30 tubular membrane, manufactured by Membrane Products Kiryat Weizman, was chosen for the tests (see Table 2).

Table 2  
Specifications for the MPW SelRO MPT-30 membrane

Configuration	Tubular
Tube diameter	12,5 mm
Membrane area (TM 410 module)	0,9 m <sup>2</sup>
Operating pressure: maximum	4 MPa
recommended	3 MPa
Operating temperature: maximum	70°C
recommended	40°C
Operating pH range: short exposure	0,5 to 13
continuous use	0,5 to 12
Retention: Glucose (180 g/mol)	75%
Sucrose (342 g/mol)	95%
5,0% sodium chloride	10%
0,2% calcium chloride	50%
Water flux at 3 MPa, 25°C	140 l/m <sup>2</sup> .h

### Definitions

$$\text{Flux [l/m}^2\text{.h]} = \frac{\text{permeate flowrate [l/h]}}{\text{membrane area [m}^2\text{]}} \quad (1)$$

$$\text{Solute retention [\%]} = \left( 1 - \frac{\text{permeate concentration}}{\text{retentate concentration}} \right) \times 100 \quad (2)$$

$$\text{Solute recovery [\%]} = \frac{\text{permeate concentration} \times \text{volume}}{\text{feed concentration} \times \text{volume}} \times 100 \quad (3)$$

$$\text{Water recovery [\%]} = \frac{\text{permeate volume}}{\text{feed volume}} \times 100 \quad (4)$$

$$\text{Solute removal [\%]} = 100 - \text{solute recovery [\%]} \quad (5)$$

Equation 2 is an approximation which is suitable when the volume of the permeate is small in comparison with the volume of the retentate (Weintraub and Loeb, 1975). Point retention is determined using instantaneous feed and permeate concentrations, whereas overall retention is determined from the initial feed concentration and composite permeate concentration.

### The pilot plant

Based on the results of the laboratory work by Wadley and Buckley (1991), a pilot plant investigation was initiated, with the following aims:

- Determine the suitability of nanofiltration for brine recovery.
- Determine the effects of temperature, pressure, flow rate and period of contact on the flux and quality of permeate and thereby set optimum operating conditions.
- Determine the extent of membrane fouling and develop pretreatment and cleaning procedures.
- Determine the suitability of the recovered brine for recycle and the make-up salt requirements.

- Obtain an estimate of membrane life under the proposed operating conditions.
- Gather sufficient data to enable design of a full-scale plant.

Pilot plant tests were carried out using a 1,2 m module containing eighteen 12,5 mm diameter SeIRO™ MPT-30 tubular membranes, on a plant which was designed and constructed by Tongaat-Hulett Sugar Ltd. Figure 3 is a flow diagram of the pilot plant. The plant was equipped with high pressure, high temperature and low level trips. The operating pressure and flow rate were manually controlled by adjusting needle valves 1 and 2. The operating temperature was regulated by setting the cooling water flow manually and allowing the temperature controller to “trim” to the setpoint by means of the feed tank heater. The cooling coil was necessary since a temperature rise occurred across the high pressure system.

### Experimental method

Eight batch concentration runs were undertaken. Feed for the first four runs comprised 100 l composite batches obtained by taking equal volume samples at fixed intervals throughout a regeneration cycle. The remaining four runs were carried out on feed samples similarly obtained from the salt-rich fraction. The standard conditions for the batch concentrations were a pressure of 3 MPa and a circulation

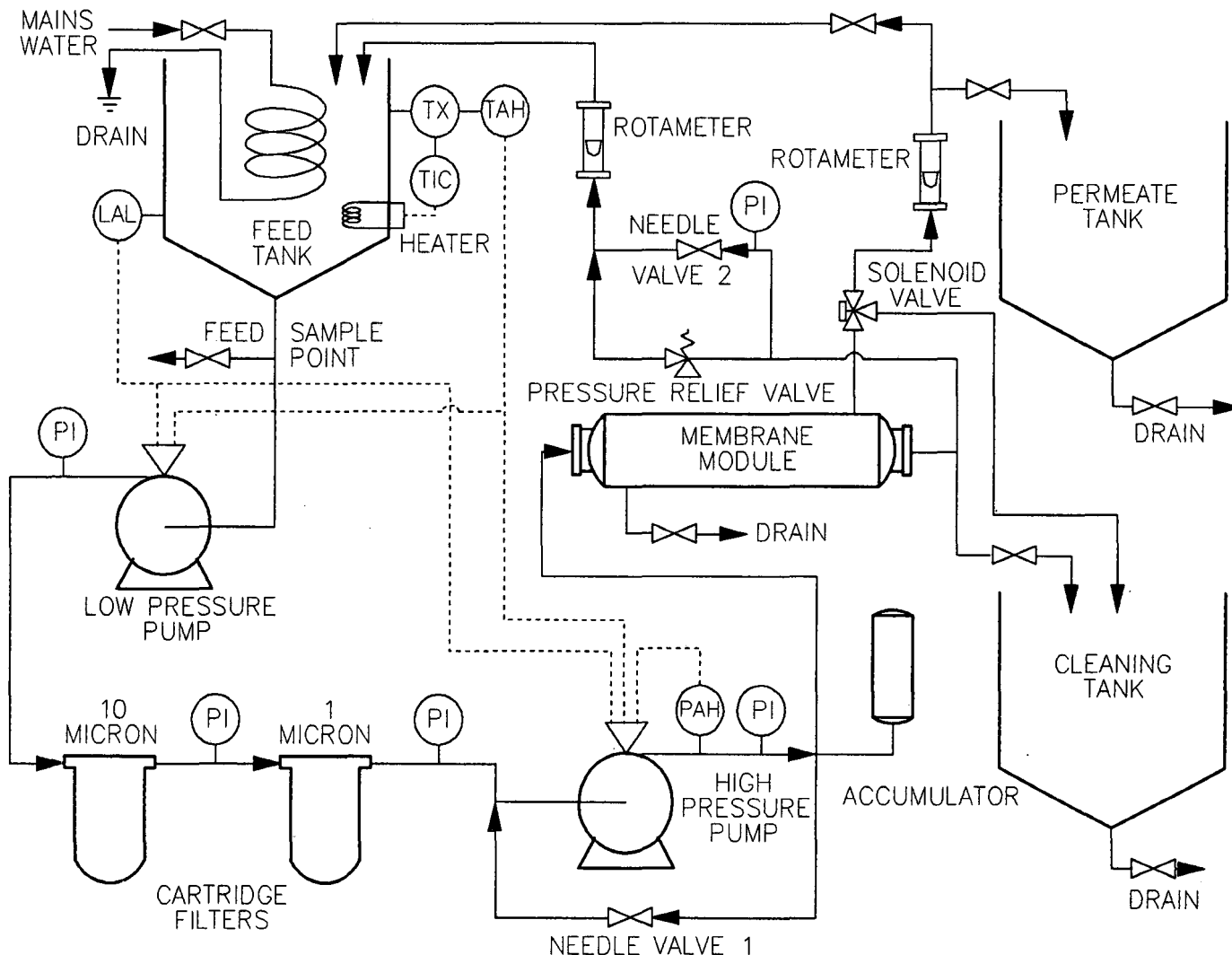


FIGURE 3 EFD of the nanofiltration pilot plant

flowrate of 13,5 l/min. Four of the runs were carried out at an operating temperature of 45°C and the remaining four runs at 60°C.

The plant was operated in the total recycle mode (both retentate and permeate returned to the feed tank) until the desired operating temperature was attained. Batch concentration was then commenced, with the permeate being collected in the permeate tank. Each run was continued until equipment constraints prevented further water recovery.

Continuous recycle runs (fouling rate tests) were performed by batch concentrating a 200 l sample to the desired feed concentration, before switching to total recycle. The plant was then run continuously for a period of five days, with readings and samples being taken daily. The level in the feed tank was made up with distilled water each day to correct for evaporation.

Whenever two or more days had elapsed between runs, the membrane was sequentially cleaned before the run. This comprised a water cycle, a cycle with 0,5 % Na<sup>4</sup>-EDTA and a further water cycle. When less than two days had elapsed, a water cycle only was performed. The water used for all cleaning was evaporator condensate (normally recycled as boiler feedwater). When the plant was to be left standing for more than two days, the module was filled with a 0,1% solution of sodium metabisulphite to inhibit microbiological activity.

### Sample analysis

Samples of the retentate and the permeate were analysed for conductivity, pH, chlorides and total carbon. Total carbon (TC) and inorganic carbon (IC) analyses were carried out using a Beckmann Model 915B Total Carbon Analyser. Samples from the first four runs were analysed for IC, however it was found that the IC was low compared to the TC (less than 10%), so it was subsequently omitted.

Samples from the first two runs were also analysed for absorbance at 420 nm and Chemical Oxygen Demand (COD). The absorbance and COD values did not correlate well with the TC values. The absorbance values are strongly dependant on pH and do not allow determination of the concentration of colourless organic compounds. The COD measurements are inconsistent since they are strongly affected by chloride concentration. The TC was a reliable and easily obtained measure of the organic matter content of the samples.

## Results

### Solute retention

A summary of the retention data from all the batch runs is presented in Table 3.

Table 3  
Retention Data Summary

	NaCl retention (%)		TC retention (%)	
	Point	Overall	Point	Overall
Minimum	-2	1	71	71
Maximum	15	9	93	88
Average	9	4	87	81

The TC retention was lower at higher temperatures and higher initial feed TC concentrations. The latter observation may be attributed to variations in the molar mass distri-

butions of the feed samples. It may be concluded that samples with higher TC concentrations contained proportionally more lower molar mass compounds. It was also observed that the TC retention increased slightly during each batch run. This is due to the permeation of low molar mass organic species resulting in a gradual increase in the average molar mass of the feed.

Retention of sodium chloride was found to decrease significantly with increased sodium chloride concentration and to decrease slightly with increased temperature. An additional marked effect was a decrease in sodium chloride retention at higher total carbon concentrations (Figure 4). The negative retention of sodium chloride obtained in one of the runs may be attributed to this phenomenon. This effect may be accounted for by the enhancement of the passage of sodium chloride ions through the membrane due to the presence of charged organic molecules.

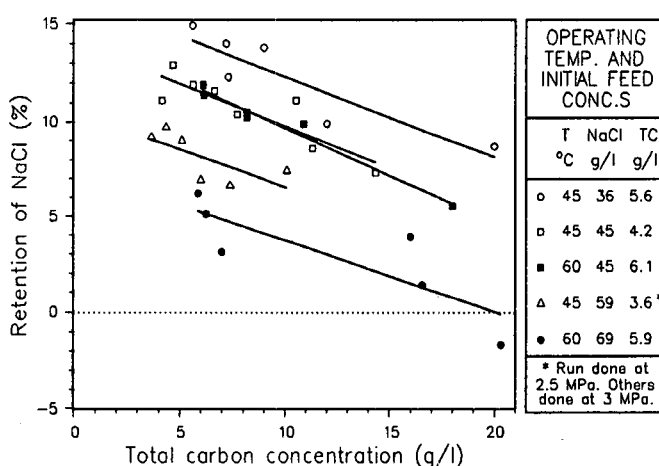


FIGURE 4 Dependence of NaCl retention on TC concentration

### Recoveries

Figure 5 illustrates the dependence of three important process variables on water recovery. Although increasing the water recovery would increase the sodium chloride recovery, this would be at the expense of decreasing the flux and the total carbon removal. A summary of the water and sodium chloride recoveries and total carbon removals attained in the batch concentration runs is given in Table 4.

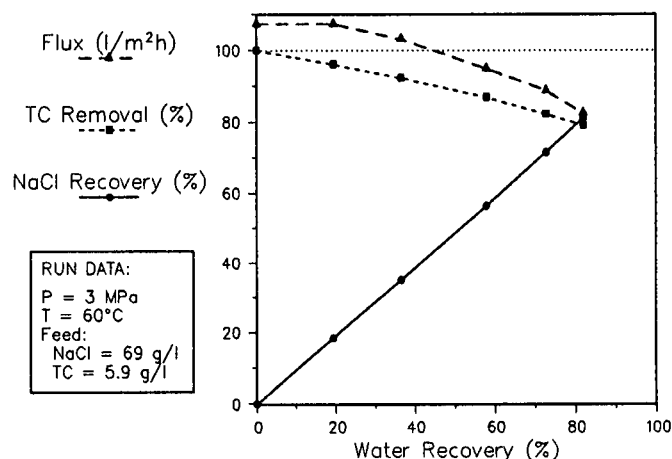


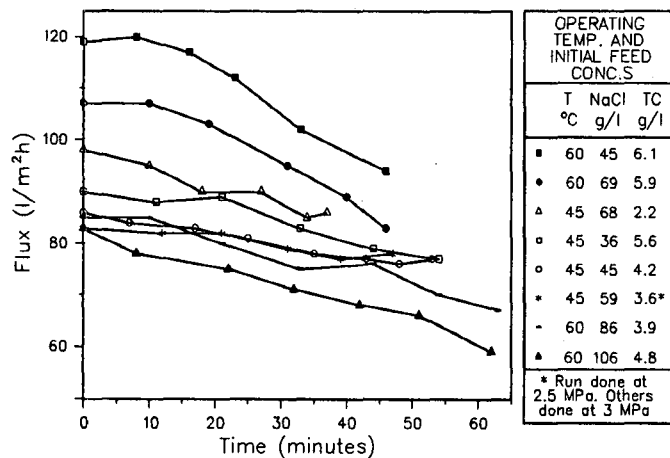
FIGURE 5 Dependence of process variables on water recovery

**Table 4**  
**Recovery Data Summary**

	Water recovery (%)	NaCl recovery (%)	TC removal (%)
Minimum	69	64	79
Maximum	83	81	89
Average	74	71	85

**Flux**

The flux decline over the period of a batch run (35 to 65 minutes) was, on average, 11% for the runs carried out at 45°C and 23% for those at 60°C. This marked difference suggests that the flux is strongly influenced by the polarised layer at the membrane surface. This layer is expected to offer a greater resistance at higher temperatures due to the increased flux and the accompanying increased rate of transport of solutes to the membrane surface. Hence, the beneficial effect of elevated temperature on flux is partially offset by the increased retarding effect of the polarised layer. The flux decline during each batch run is shown in Figure 6. The dependence of flux on temperature and initial sodium chloride and total carbon concentration is evident.



**FIGURE 6** Flux decline during batch concentrations

Cleaning of the membrane was successful in all cases, restoring the flux on pure water to the manufacturer's specification. This suggests that if any fouling occurred, it was reversible.

**Flux correlation**

In order to quantify the effects of operating conditions on flux, a relationship was derived by multilinear regression between flux and temperature, pressure, sodium chloride concentration and total carbon concentration, based on the full set of batch concentration data. The relationship is intended to allow performance prediction for future test work and design purposes. However, the relationship is empirical and is limited to the specific membrane and effluent tested, and to the operating ranges in which the runs were performed. These ranges are:

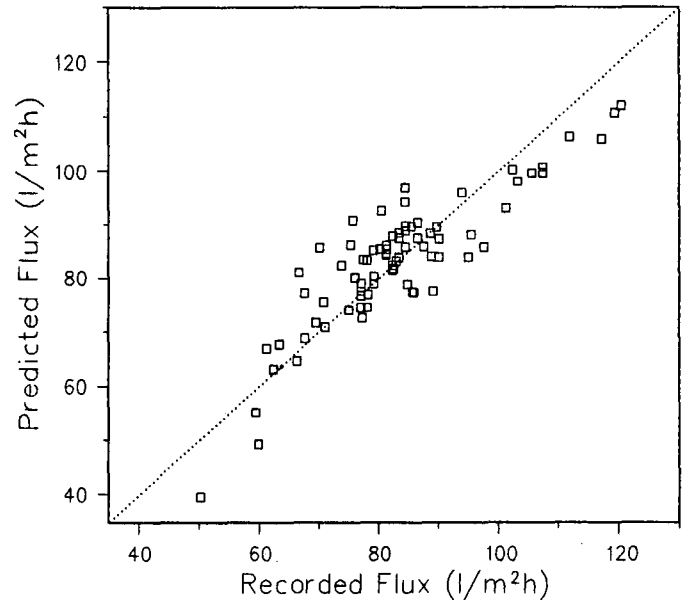
- Temperature : 25 to 65°C
- Pressure : 2,5 to 3 MPa
- Sodium chloride concentration : 30 to 120 kg/m<sup>3</sup>
- Total carbon concentration : 1 to 20 kg/m<sup>3</sup>

The derived relationship is given by the following equation:

$$F = 70 + 5,2.P + 0,015.T^2 - 0,0036.S^2 - 8,8.C^{0.5}$$

- where F = flux [l/m<sup>2</sup>.h]
- P = pressure [MPa]
- T = temperature [°C]
- S = NaCl concentration [kg/m<sup>3</sup>]
- C = total carbon concentration [kg/m<sup>3</sup>]

Figure 7 shows the relationship between actual and predicted flux for all batch run data. The dotted line represents a 1:1 relationship.



**FIGURE 7** Relationship between predicted and recorded flux

**Continuous recycle runs**

This phase of the pilot plant test work is currently in progress. In the two continuous runs done to date, the fouling that occurred over a 5-day period had no significant effect on the retention of sodium chloride or total carbon. The decline in flux with time for one of the runs is shown in Figure 8. Fouling reduced the flux to two thirds of its initial value after 22 hours, and a steady state flux of one half of the initial value was reached after 62 hours. Fouling appeared to be reversible, as sequential cleaning restored water flux to the manufacturers' specifications. Reliable projection of design fluxes, optimal cleaning frequencies and membrane life will depend on the results of further continuous runs.

**Permeate quality**

An appropriate measure of the permeate quality is its effect on the efficiency of regeneration of the loaded resin. Two pilot plant ion exchange columns were loaded in parallel to the full-scale ion exchange columns. The batches of permeate produced from the nanofiltration tests were made up to the same salt concentration and pH as the fresh brine and used to regenerate one of the pilot columns. The degree of decolourisation of the sugar liquor passing through each column was measured. The average colour removal over the 15 cycles performed to date was 70,7% for both the column regenerated using fresh brine and the column regenerated using permeate.

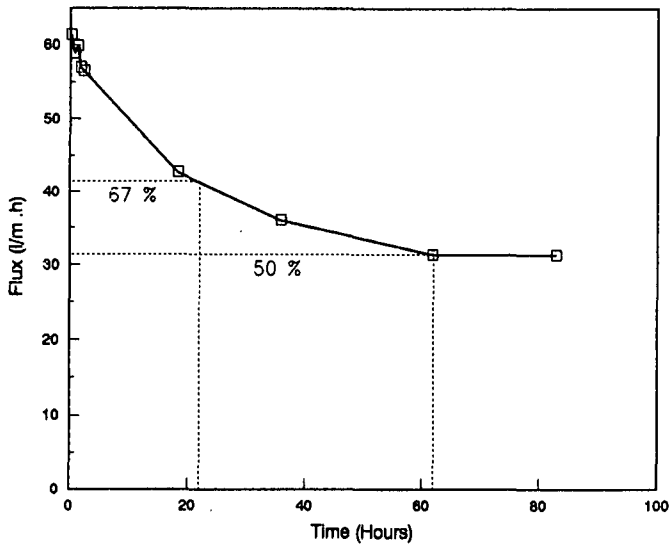


FIGURE 8 Flux decline with time

**Discussion**

*Technical evaluation*

The results of the pilot plant work to date show membrane performance to be predictable and consistent. The choice of nanofiltration resulted in acceptably high salt recovery and total carbon removal. The optimum water recovery for a

full-scale operation depends on a trade-off between sodium chloride recovery, total carbon removal and flux. While the principal aim of this work was to recycle the salt, the process has the added benefit of reducing the volume of effluent requiring disposal. This would facilitate secondary treatment of the effluent.

*Mass balance considerations*

Figure 9a depicts the sodium chloride and water mass balance for a single regeneration under the existing system. Figure 9b presents the modified balance for the regeneration system if a full-scale brine recovery membrane plant were included to treat the salt-rich fraction. In order to maintain the water balance, while recycling the maximum quantity of permeate, part of the recycled rinse water is used to make up the saturated brine. The sodium chloride concentration of the permeate depends on the feed concentration. In the proposed flowsheet, the concentration of the permeate is taken as 80 g/l, which was the average concentration of the permeate from all runs on samples from the salt-rich fraction.

*Economic evaluation*

From mass balance considerations, a full-scale plant treating only the salt-rich fraction would result in a 60% reduction in salt consumption and a 30% reduction in disposal costs for the regeneration waste stream at this refinery. In addition, water usage on the ion exchange plant would be reduced by 30%. The size of the plant (membrane area) and therefore its capital cost depend on the average design flux, while operating costs depend on the frequency of membrane

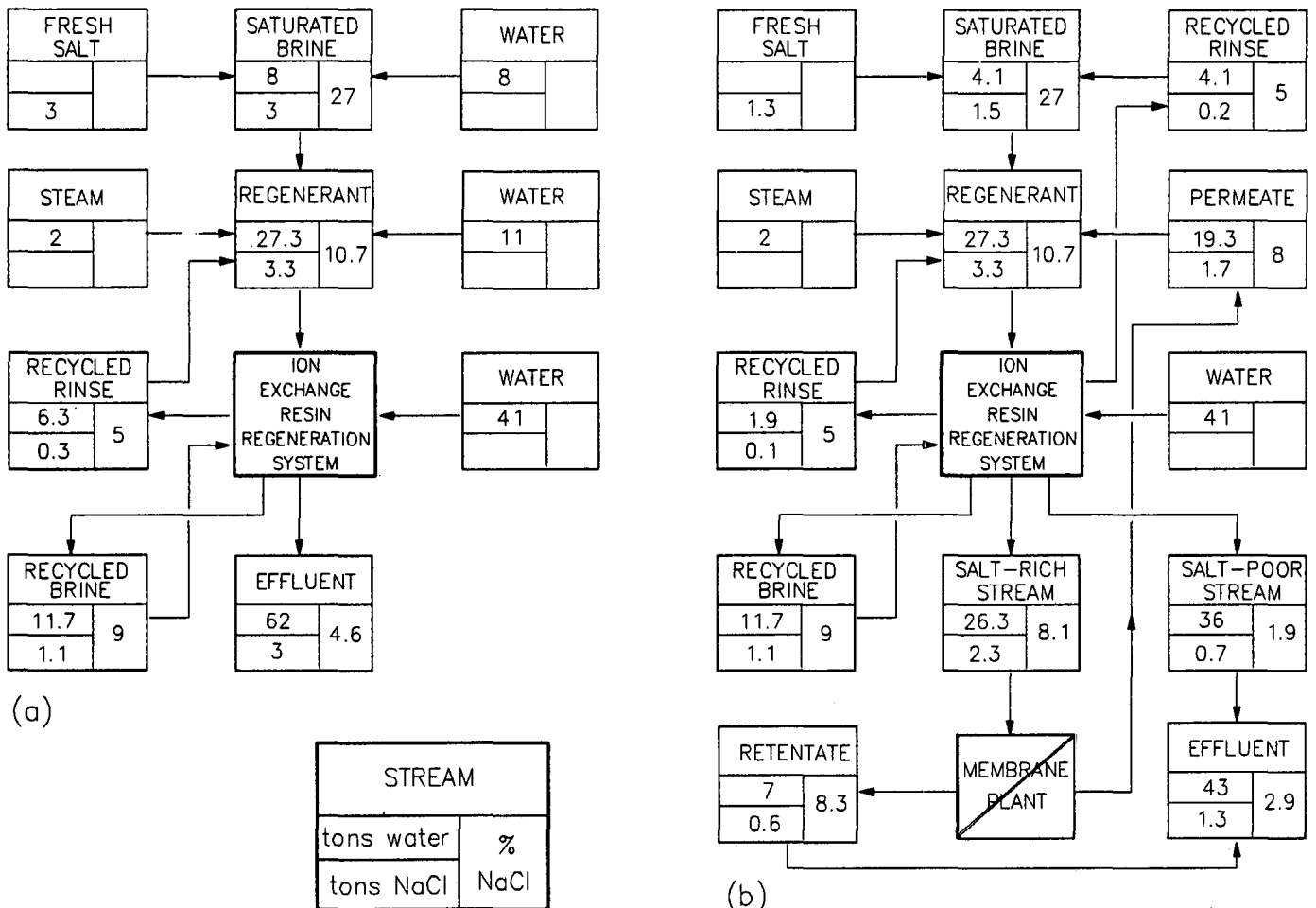


FIGURE 9 Change in the regeneration mass balance due to the inclusion of a brine recovery membrane plant  
 (a) existing regeneration system  
 (b) system with brine recovery

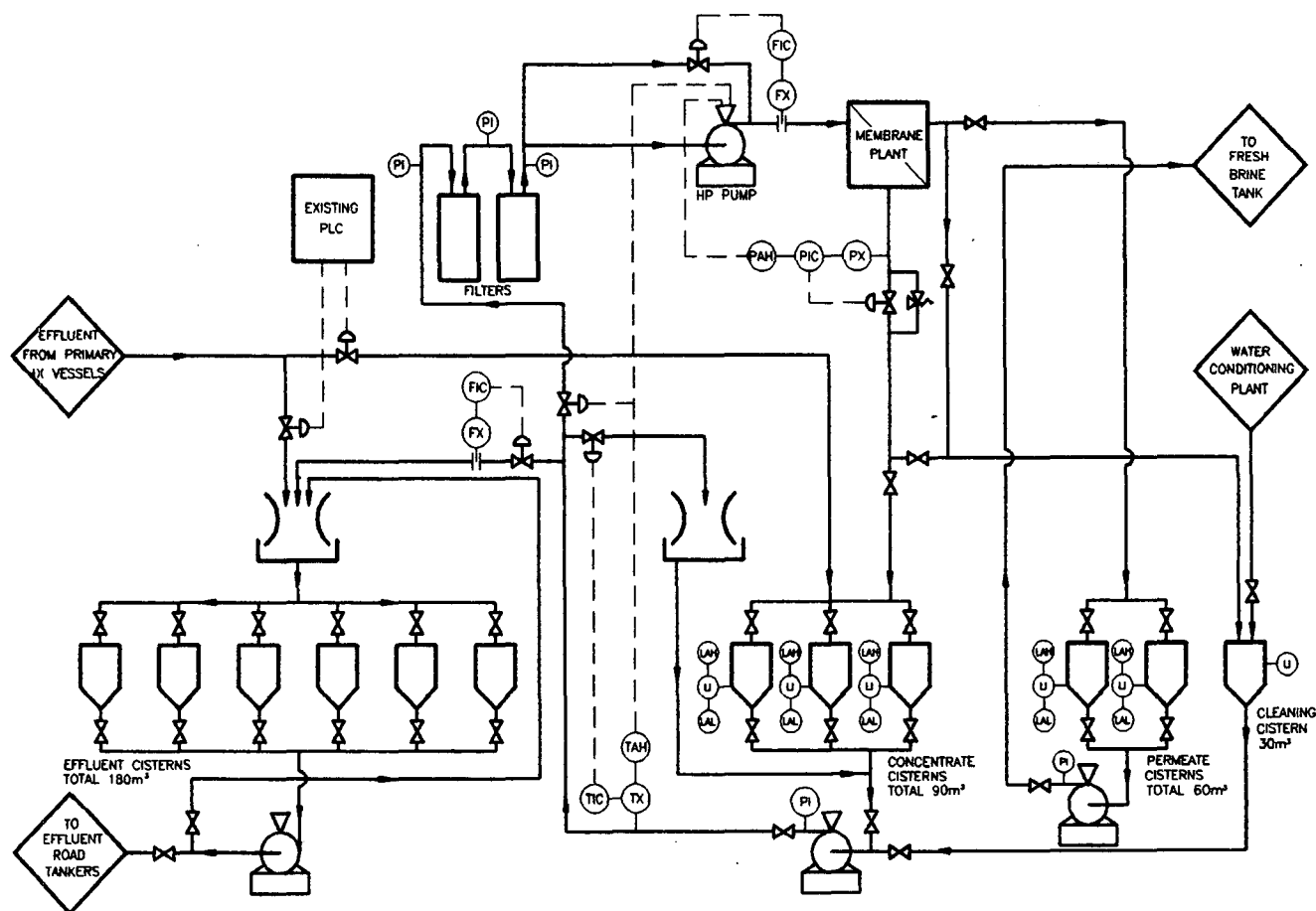


FIGURE 10 EFD of proposed nanofiltration plant

replacement (membrane life). Assuming a conservative design flux of 70 l/m<sup>2</sup>.h and a membrane life of 1 year, the plant would have a payback time of 24 months.

#### Integration into ion exchange plant

Figure 10 is a flow diagram of a full-scale nanofiltration plant incorporated into Hulett Refineries operations. The effluent is currently cooled by means of a small fibreglass cooling tower and a similar tower is proposed to cool the membrane plant feed (the salt rich fraction). Cartridge filters are included for prefiltration. The low solids loading in the effluent will ensure that cartridge cleaning and replacement requirements are low. A water conditioning plant, such as an activated carbon filter, is necessary to remove free chlorine from cleaning water, as this is not tolerated by the membrane. An alternative would be to use condensate.

#### Conclusions

The investigation has indicated that the use of nanofiltration is suitable for the recovery of part of the brine from the ion exchange resin regeneration effluent and does not lead to a decrease in sugar liquor decolourisation efficiency. This process at Hulett Refineries would result in a 60% reduction in salt consumption and a 30% reduction in effluent volume.

#### Acknowledgements

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