BAYER LIQUOR PURIFICATION BY NANO-FILTRATION MEMBRANES

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Abstract

A paper presented by QAL at AQW 2002, examined the viability of nano-filtration (NF) membranes for the purification of Bayer liquor. In flat-sheet, cross-flow configuration, the durability, flux and rejection characteristics of the membranes were indicative of potential economic value. The current paper reports recent work to further assess the benefits and risks associated with a potential NF membrane process for use in a Bayer refinery.

Pilot trials were conducted using spiral-wound NF elements, this configuration commonly offering an acceptable compromise between membrane density (capital cost) and fouling rate (operating and capital cost). This enabled development of a flow sheet for a membrane plant that would produce retentate for feed to a downstream organics-removal process, and permeate for return to the washer train.

A low level of permeate flux was found to necessitate relatively high membrane area, while poor recovery necessitated a high level of recycle within the membrane plant. Both factors imposed significant additional capital and operating cost when compared to conventional applications (eg water treatment).

Due to fouling of the membrane, permeate flux declined at a rate of 0.1% per hour. Flushing with water, dilute caustic or dilute acid, returned the permeate flux to approximately 90% of it's level at the start of each cycle, thus partially arresting the overall fouling rate. In terms of a full-scale plant, the high fouling rate imposed significant additional capital and operating costs.

1 Introduction

Membranes are semi-permeable barriers that selectively allow the passage of molecules, dissolved ions and particles. In this way they split a feed stream having a given impurity level, into separate discharge streams of lower and higher impurity levels. The applications of membranes in industrial processes are diverse and include, for example, municipal water treatment, desalination and acid and caustic recovery.

In the Bayer process various processes – for example wet oxidation (Rosenberg, 2000), biological degradation (Chinloy et al, 1993), or disposal of liquor with mud residue – may be used to control liquor-organics levels. It has been proposed that membranes could be used to pre-concentrate the feed streams to these processes, thus reducing their capital and operating costs (Armstrong et al, 2002a; Armstrong et al, 2002b). Membrane separation potentially offers the additional benefit of differential concentration, i.e. concentration of organics to a greater relative extent than soda, and thus enabling organics removal at a lower soda penalty.

A cost-benefit analysis of a proposed membrane plant would therefore include assessment of the capital and operating costs of the membrane plant itself, as well as those of the downstream plant or process. The substantial costs of the membrane plant may be justified if the capital and operating costs of the stand-alone downstream process were sufficiently reduced. The additional savings that could result from decreased soda loss, could make a marginal or cost neutral combination viable.

This paper reports results from continuous-flow testing of spiral-wound NF membranes, treating Bayer plant seed-wash filtrate. Membranes from various manufacturers were tested, and the resulting data was used to determine the technical and economic viability of a membrane process at QAL.

2 Membrane characterisation

In general, membranes are characterised by their molecular weight cutoff (MWCO), i.e. the molecular weight at which 90% of a given species is rejected by the membrane. Figure 1 provides approximate MWCOs for the four main categories of membrane. At the coarsest end of the size continuum, micro-filtration (MF) is used to separate, for example, paint pigments or bacteria. At the other end of the size continuum, reverse-osmosis (RO) membranes are used for water purification and desalination. Between the extremes of MF and RO lie ultra-filtration (UF) and nano-filtration (NF). It is the latter that, through appropriate MWCO and recent advances in caustic resistance, now have potential for application in the Bayer process.

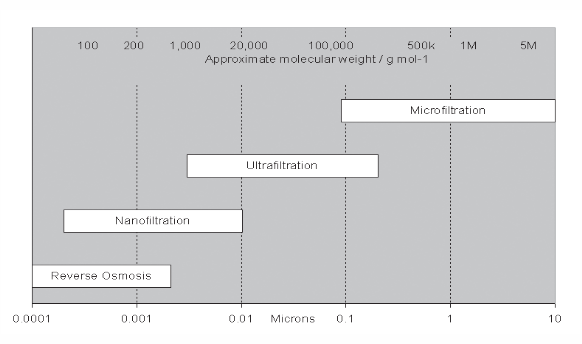

Figure 1. Approximate pore size and molecular weight cut-off (MWCO) for various membrane types.

Work previously conducted at QAL included performance testing of various polymer-NF membranes in synthetic Bayer liquor (Armstrong et al, 2002). The tests were conducted in a small-scale cross-flow membrane cell, with the membrane configured as a flat sheet. In cross-flow mode the retentate sweeps suspended solids away from the membrane surface thus minimising the rate of fouling. It was concluded that separation performance and durability, at low to medium free caustic feed levels, would likely give economic return if the membrane process was used as a precursor to wet oxidation, biological degradation or disposal with mud residue.

Flat sheet configuration is however characterised by relatively low packing density and hence capital costs are high for a given membrane area. In many industrial applications spiral-wound membrane elements (Figure 2) offer greater packing density than flat sheets, and hence are a lower capital cost alternative. Spiral-wound membrane elements also offer increased turbulence at the membrane surface (Wagner, 2001), thereby further reducing fouling rate and concentration polarisation, and thus increasing the average permeate-flux and rejection.

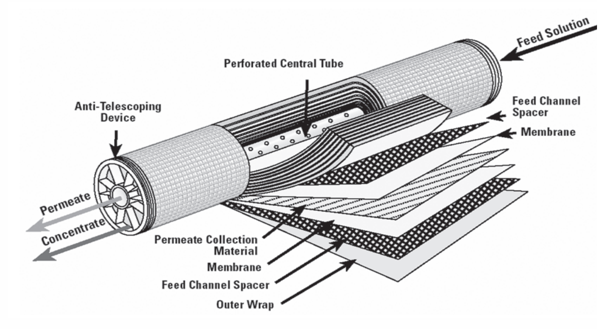

Figure 2. Spiral-wound membrane element (reproduced from Wagner, 2001).

A process flow diagram of a membrane plant to treat Bayer liquor is shown in Figure 3.

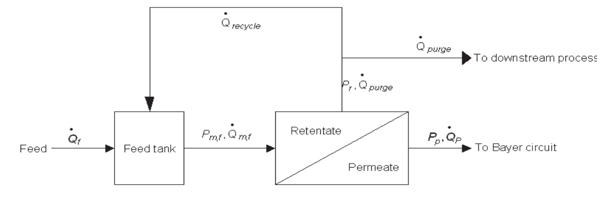

Figure 3. Process flow diagram of membrane process in Bayer plant.

Note the recycle stream and the fact that a portion of it is bled from the membrane plant at a rate ($\dot{Q}_{purge}$) defined by the various downstream processes. Permeate flow rate ($\dot{Q}_P$) is then defined by the overall flow balance,

$$\dot{Q}_f = \dot{Q}_P + \dot{Q}_{purge} \tag{1}$$

where $\dot{Q}_f$ is the flow of feed liquor to the membrane plant. The required membrane area (A_{mem}) is determined from the ratio of permeate flow, to permeate flux (F_p),

$$A_{mem} = \frac{\dot{Q}_p}{F_p} \tag{2}$$

Permeate flux is a function of *net driving pressure* (*NDP*) and temperature, and of the feed liquor composition, and is determined by pilot testing. Net driving pressure is the average pressure available to drive liquid through the membrane, and is defined by,

$$NDP = \frac{(P_{mf} + P_r)}{2} - P_p \tag{3}$$

where P_{mf}, P_r and P_p are the membrane feed pressure, retentate backpressure and permeate backpressure. *Recovery* is defined as the ratio of permeate flow (i.e. $\dot{Q}_P$) to membrane feed flow ($\dot{Q}_{mf}$),

$$Recovery = \frac{\dot{Q}_p}{\dot{Q}_{mf}} \tag{4}$$

and is a function of permeate flux and *NDP*, and again is measured by pilot testing. The recovery effectively defines the recycle flow rate ($\dot{Q}_{recycle}$) and is, along with the membrane area, a key parameter in establishing the plant cost. *Rejection* is defined as the ratio of the concentration of a liquor component *i* in permeate ($c_{i,p}$), to that in membrane feed ($c_{i,mf}$),

$$Recovery = \frac{\dot{Q}_p}{\dot{Q}_{mf}} \tag{5}$$

Rejection and recovery together determine the steady state levels of impurity or soda in the recycle stream, and thus in the stream sent to the downstream process.

3 Experimental

A simplified process-flow diagram of the pilot-scale test rig used in this work is shown in Figure 4. Liquor was supplied from a 250 L polypropylene feed tank to a stainless-steel low-pressure centrifugal pump (maximum 4500 kPa) and thence to a pair of 20-inch cartridge filters (CUNO Microkleen). The resulting filtered liquor was directed to either a high-pressure positive displacement pump (maximum 6900 kPa), or back to the feed tank via a plate heat exchanger. Liquor temperature was monitored at the feed tank discharge, and controlled by automatically adjusting the flow of hot water to the heat exchanger.

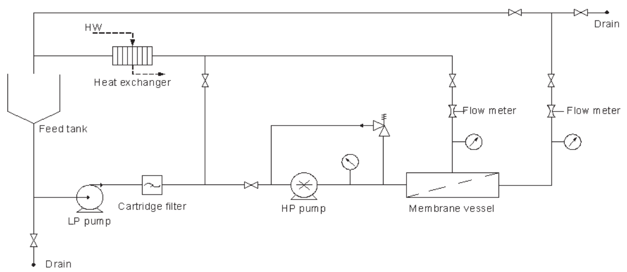

Figure 4. Diagram of membrane pilot-test rig.

High-pressure liquor was fed, via a pulsation dampener, to a horizontally mounted, single element, stainless steel membrane vessel from which permeate and retentate streams were discharged. Gate valves in the retentate discharge lines controlled backpressure at the membrane. The retentate stream was returned, via the heat exchanger, to the feed tank. The permeate stream was returned directly to the feed tank, or discharged to drain. Permeate and retentate flows were measured by rotameter.

The spiral-wound membrane elements were 40 inches long by 4 inches in diameter, and utilised a conventional brine seal. Each new element was flushed of preservative as per the manufacturers' instructions. The rig was then hydrostatic tested to ensure it was leak-free. Flow rate was measured at a range of trans-membrane pressures, before discharging the water to drain.

Seed wash filtrate was then transported from the plant and decanted into the feed tank. To ensure minimal solids in the membrane feed, solids were settled in the feed tank for 30 minutes before discharging approximately 50 L of solids and liquor from the bottom of the tank, to the drain. Further seed wash filtrate was decanted into the feed tank and the settling procedure was repeated. During start-up and preheating, the liquor was circulated through the pre-filtration loop until the measured solids concentration was less than 10 mg L^{-1}.

After achieving the desired level of solids in the feed liquor, the low-pressure feed was diverted to the inlet of the high-pressure pump. The membrane housing was then pressurised and permeate and retentate backpressure were adjusted to achieve the desired *NDP*. Flow and pressure were allowed to stabilise for a few minutes prior to recording the relevant process parameters. Samples of feed, retentate and permeate were analysed for total organic carbon, alumina, caustic, soda and oxalate. This was repeated at a range of *NDP* and the resulting data were used to determine recovery and rejection.

To simulate the continuous process – with its inherent recycle and build-up of impurities levels – defined quantities of permeate were discharged from the test batch. The *volume reduction factor (VRF)* was defined as the ratio of the initial volume of the liquor batch (V_{in}), to the final volume of the liquor batch (V_f),

$$Recovery = \frac{\dot{Q}_p}{\dot{Q}_{mf}} \tag{6}$$

4 Pilot-scale testing of new spiral-wound NF membranes

Figure 5 summarises permeate-flux, NOOC (non-oxalate, organic carbon) rejection, and soda rejection, for seven commercially available membranes. On the basis that it offered the highest levels of permeate flux and NOOC rejection, and an acceptably low level of soda rejection, membrane '7470' was selected for further testing.

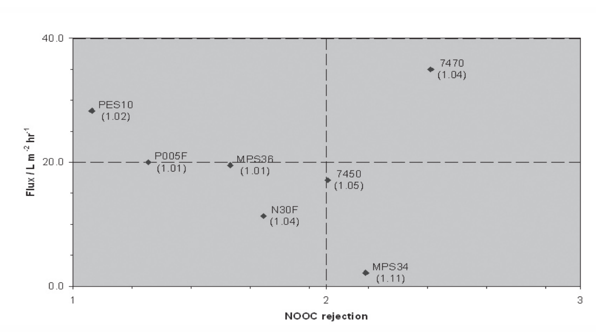

Figure 5. Flux, NOOC rejection and soda rejection (bracketed value). Data obtained from pilot testing of seven commercially available membranes, processing seed-wash filtrate.

For each of three previously unused 7470-membrane elements – all of which were obtained from a single manufacturing batch – the process-water flux was measured at a range of *NDP*. The data demonstrate minimal variation in flux levels between the three membranes (Figure 6).

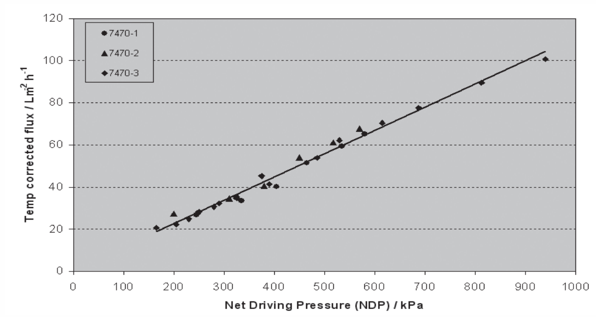

Figure 6. Permeate flux vs. net driving pressure. Data obtained from pilot testing of three '7470' membranes (obtained from a single manufacturing batch), processing water only.

The membranes were then exposed to seed-wash filtrate (18 g/L caustic, 5 g/L alumina) at a range of NDP and VRF. The average permeate flux was approximately 50% of that of process water, and was independent of VRF (Figure 7). Recovery was 6–10% (cf water, 15–65%) and was found to increase by approximately 1% per 100 kPa increase in NDP. The process-water flux pre and post seed-wash filtrate were found to be the same, indicating minimal fouling during the relatively short (3 hr) campaigns.

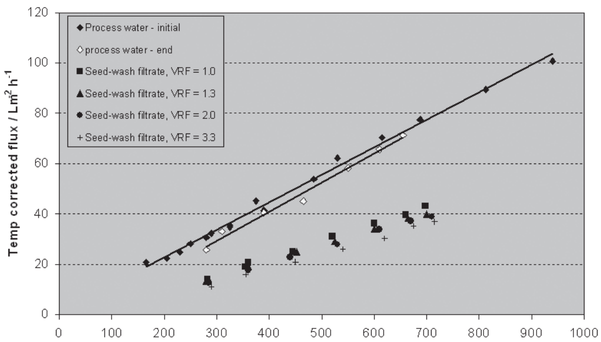

Figure 7. Permeate flux vs net driving pressure. Data obtained from pilot testing of membrane '7470-1', processing seed-wash filtrate.

Average NOOC rejection was 64% and was dependent on the NOOC concentration in the feed (Figure 8). Average soda rejection was 3% and was independent of the soda concentration in feed. On this basis, to maximise NOOC concentration and NOOC/soda ratio in the discharge, the recycle rate would be maximised.

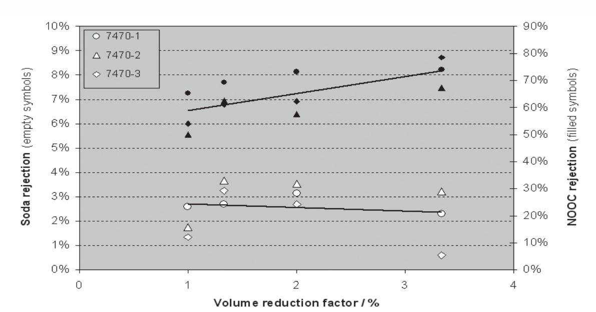

Figure 8. Soda and NOOC rejection vs. volume reduction factor. Data obtained from pilot testing of membrane '7470-1', processing seed-wash filtrate.

To maximise the recycle rate at a given permeate flow, relatively high membrane area and low *NDP* would be utilised. This is the converse of the membrane desalination process, in which recycle is small, the purity of the resulting permeate is high, and a discharge stream only slightly enriched in impurities is returned to the environment. Relative to membrane desalination, the Bayer application would be characterised by higher flow at lower pressure, and higher membrane and piping costs (to accommodate the high recycle).

5 Pilot-scale testing of aged spiral-wound NF membranes

The capital cost of a membrane plant is proportional to the installed membrane surface area. Over the life of a membrane the permeate flux will decline due to membrane fouling and will, on average, be substantially less than that of a new membrane. The rate of decay of permeate flux, and thereby the average permeate flux, must therefore be measured in order to accurately assess capital and operating costs.

Medium-term tests were conducted to establish the fouling characteristics of the 7470 membrane in semi-continuous operation, and thereby to determine the likely average permeate flux. Membrane '7470-1' was chosen as the candidate and was subjected to seed-wash filtrate, at 30% volume reduction factor, on day-shift operation. After each cycle of operation, process water was used to flush the test rig.

Figure 9 presents the permeate flux as a function of membrane age over approximately 2 months. Over the short term, permeate flux declined at a rate of approximately 0.13% per hour. After 190 hrs processing seed-wash filtrate, process water flushing (2hrs, 60°C) returned the seed-wash filtrate permeate flux to 92% of its initial level.

Caustic cleaning (minimum 2 hrs, 60°C, 40 g/L caustic) did not recover the initial flux. Sulphuric acid washing (9 hrs, 30°C, pH 1.3) also did not recover the initial flux. The average permeate flux over 2 months (~1500 hrs) was approximately 60% of that of the new membrane.

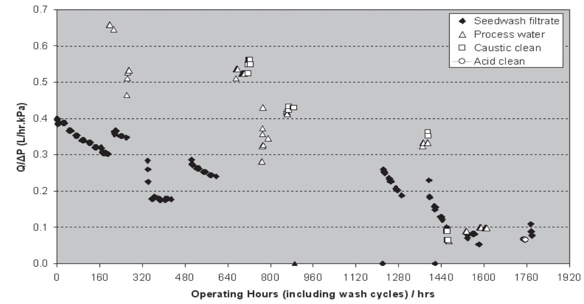

Figure 9. Normalised flux vs. operating time. Data obtained from pilot testing of membrane '7470-1', processing seed-wash filtrate.

Such rapid fouling of the spiral-wound membrane element prevented the direct assessment of durability (the long term mechanical stability of the membrane), which for membranes in the flat-sheet configuration had previously exceeded 100 days (Armstrong et al, 2002). A membrane autopsy conducted by a third party suggested that fouling was mainly the result of flow restrictions due to blockage by gibbsite particles in the feed channels of the spiral element, and that mineral scaling of the membrane surface was minimal. This appears an unlikely mechanism however, as gibbsite would be sufficiently soluble under such conditions to fully dissolve in the available caustic or acid.

A more likely mechanism may be that of pore blockage through the growth of molecular-scale deposits, or the chemical modification of the membrane. Supporting the latter hypothesis, the autopsy made note of the unexpected brittleness of the used membrane, and ascribed this to the cycling of pH associated with periodic acid cleaning.

6 Economic evaluation

On the basis of the performance data obtained by testing new membranes, the capital cost of a full-scale membrane plant to treat 250 kL/hr of seed-wash filtrate was estimated to be at least triple that of a conventional (eg desalination) NF plant treating the same amount of feed. The main factor in the high cost was low recovery, which necessitated excessive membrane area and additional piping and tankage to accommodate the recycle stream.

To offset the rapid fouling and its affect on the average flux, the installed membrane area and/or the frequency of membrane replacement, could be increased. It was estimated that at the optimum levels of membrane area and membrane replacement frequency, a capital-cost multiplier of 1.5 would be applied. The overall capital cost was therefore estimated to be about five times that of a conventional NF plant treating an equivalent amount of feed.

The operating expense – including pumping, maintenance and periodic membrane replacement – was estimated to be approximately 50% of the base capital, per annum. On this basis the overall cost exceeded, by a substantial margin, the benefits that would be obtained by concentrating feed to a downstream process and/or through soda savings.

7 Conclusions

Pilot-scale testing of spiral-wound nano-filtration membranes was conducted at QAL using seed-wash filtrate as feed. Of the six membranes tested, type '7470' apparently offered the best combination of organic rejection, soda rejection and recovery. Recovery was, however, considerably less than would be the case for a conventional membrane plant (for example desalination). Consequently the capital cost was high relative to a conventional plant.

Further increasing the capital cost, and contributing significantly to the operating cost, was the rapid and irreversible fouling of the spiral wound membrane elements. Water, caustic and acid cleaning did not arrest the rate of fouling, thus suggesting that fouling was not a consequence of gibbsite scale. An alternative mechanism may have been the chemical modification of the membrane surface such that it's porosity was effectively reduced.

On the basis of the anticipated capital and operating costs, and benefits determined in the context of the QAL Bayer circuit, membrane liquor purification did not meet the required economic return.

References

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