# A NEW MEMBRANE PROCESS TO PURIFY BAYER LIQUORS

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## Abstract

Organic impurities in Bayer liquor are known to cause serious yield, quality and operational issues in plants to an extent dependant on bauxite quality and processing conditions. Various organic removal processes have been proposed but only a few have favourable economics for established application.

Recent advances in membrane technology mean certain membranes are now more amenable to use with dilute caustic streams.

This paper outlines the testing of new nano-filtration membranes for their durability in various Bayer plant liquors and their effectiveness at removing liquor impurities particularly organics. This organic removal is linked to previous work on the impact of various molecular weight fractions from Weipa bauxite on precipitation yields and product quality under typical growth and agglomeration conditions.

These results will indicate the viability of this new process application for improved liquor purity and productivity in Bayer plants.

## 1. Introduction

The presence of organic impurities in Bayer liquor represents a major problem for the refining of bauxite to alumina. Organics in liquor decrease hydrate yield by decreasing available caustic in liquor and by decreasing growth rate in precipitation. (Atkins & Grocott, 1988). Sodium oxalate particles in particular impact generation of hydrate fines and control of product sizing (Reyhani et al, 1999). Some organics also contribute to soda contamination of alumina product (Grocott & Rosenberg, 1988; Armstrong, 1993), problems with sodium oxalate crystallisation (Power & Tichbon, 1990), poor red mud settling, liquor and product coloration, liquor foaming, plant odour and scaling. (Atkins & Grocott, 1988)

The majority of the organics present in Bayer liquor come from the bauxite and are of humic origin. They react to form soluble organic sodium species, mainly during digestion, and accumulate in process liquor to concentration levels ranging from a few grams per liter up to 40g/L carbon. (Atkins & Grocott, 1988) However it is only relatively recently that detailed information has been published on the functional characteristics of these organics and the molecular weight distribution in typical Bayer plants. For example, the organic composition from a low temperature Bayer refinery (operating digestion at 145–150°C) and from QAL (with digestion at about 255°C) with different bauxite feeds have been studied in the University of Technology Sydney. (Wilson et al, 1999; Smeulders et al, 2000) The complex organic matter in bauxite is degraded by the high temperature, pressure and caustic, oxidising environment to lower molecular weight species. This produces for example simple benzene and hydroxy benzene carboxylic acids (as their sodium salts) in the less than 1.2kD molecular weight fraction in QAL liquor (< 1,200 Dalton molecular weight). Some of these are known hydrate precipitation poisons. (Grocott & Rosenberg, 1988; Armstrong, 1993) Oxalate, formate and acetate (especially the latter) are formed in relatively large quantities, particularly from high temperature digestion. Relatively small amounts of organic matter with molecular weights up to and above 300kD are still present in QAL spent liquor, and these can also have a measurable impact on hydrate and oxalate yields. (Smeulders et al, 2001)

Over the years many methods have been investigated to remove these organics. These include major processes such as liquor burning and wet oxidation. To date, none of these processes are universally attractive due to high capital investment, technical risk or operating cost.

Membrane processing is becoming more widely used in process industries for purification or clean-up of alkaline effluents. (Michaels, 1996) Previous research has proposed the use of membranes in various modes for purification of Bayer liquors but we believe none of these have been implemented to date on plant scale. (Thé & Misra, 1987; Thé & Misra, 1988; Brown & Tschamper, 1988; Brown & Tschamper, 1989A; Brown & Tschamper, 1989 B; Awadalla et al, 1994)

In recent times, membranes have been developed in the Nano-Filtration (NF) range, which are intermediate between Ultra-Filtration and Reverse Osmosis, and which also contain charged surfaces suitable for treating caustic effluents. (Simpson & Buckley, 1987; Bindoff et al, 1987) A break-through occurred recently to improve their stability in more concentrated alkaline solutions and to adapt their chemical characteristics for removal of a range of organic solutes, including lower molecular weight species (Yacubowicz et al, 1995).

This paper reports results from experimental work to determine the relative durability of ten commercial NF membranes in various caustic and caustic aluminate liquors. Low, medium and high concentration caustic liquors (20–270g/L, expressed as $Na_2CO_3$) were tested to represent the range of liquor streams available in a Bayer refinery for organics removal via membrane filtration. These results are assessed to identify process applications that are likely to be viable in Bayer plants.

## 2. Experimental

Preliminary testing at University of New South Wales indicated potential benefit from two NF membranes in treating spent liquor, but gave no indication of membrane durability during longer term operation at Bayer process temperatures (Glastras, 1999). This work also demonstrated

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that Ultra-filtration membranes gave lower separation performance for the Bayer liquors studied.

After communications with various membrane suppliers and systems manufacturers, ten flat-sheet membranes were chosen for this investigation of caustic durability and separation performance:

| Membrane Company | Membrane Product Code |
|---|---|
| Koch Membrane Systems | MPF34, MPF36 |
| Nadir Membranes (Hoechst, Celgard) | N30F, P005F, NF PES10 |
| Filmtec (Dow Chemical Group) | NF-70 |
| Desal Inc/Osmonics | DK |
| Nitto Denko (Hydranautics) | 7410, 7450, 7470 |

To determine durability and subsequent performance in Bayer liquors, each membrane was first stored in a pure caustic solution or a caustic aluminate solution at 60°C in an oven for various time periods up to five months.[1] Before storage, each membrane was pretreated as per manufacturer's guidelines by soaking in de-ionised water. After storage, membranes were tested for separation and flux performance in a flat sheet membrane rig using the equivalent caustic strength plant liquor, with Total Organic Carbon (TOC) rejection, flux rate and soda rejection being plotted versus time on a log scale. Membrane degradation is indicated by the degree of increase in flux rate and/or decrease in TOC and soda rejections.

A schematic of the flat sheet membrane rig is shown in Figure 1.

Four different synthetic liquors were used for the durability testing, at approximately 20g/L, 100g/L and 270g/L caustic concentrations. (There was concern that if actual Bayer liquors were used for durability testing, these would precipitate gibbsite and foul the membranes at the static storage conditions.) The 20g/L and one 270 g/L synthetic liquor were simply pure caustic solutions made from sodium hydroxide pellets. The 100g/L and the other 270g/L caustic aluminate synthetic liquor had aluminium wire, sodium carbonate and sodium chloride added to simulate the free caustic and certain impurities of analogous Bayer spent liquors. Only enough aluminium wire was added to obtain an aluminate concentration below the gibbsite equilibrium solubility of the liquors at 60°C, to avoid gibbsite precipitation onto the membranes during storage.

The lab flat-sheet rig was used to test the performance of each of the membranes after storage, using various plant feeds such as lime treated seed wash filtrate ("LSOF"), seed wash filtrate ("B filtrate"), and both diluted and undiluted Liquor to Digestion ("L-D").

Performance tests consisted of at least three sets of runs, each set corresponding to a different storage time for the membranes (0 – 5 months). Each of the membranes stored for that time were tested in a random order. Replicates were also performed for each time period.

At the start of each run, fresh feed liquor was collected from the plant. This liquor was pre-filtered through a 0.8 mm micro-filtration membrane and then held at 60°C in the water bath. The lines and cell in the rig were initially flushed with the feed liquor and then the test undertaken. The retentate stream was recycled back into the feed tank. Once a steady flow had been achieved, the feed pressure was increased to 1000kPa. A retentate sample was then taken, the temperature and pressure recorded and the permeate flow through the membrane was measured using a burette collection vessel. After the run was complete, the cross-flow cell and burette were rinsed and dried ready for the next test.

This work was undertaken on all membranes within each set over a few days using the same batch of feed liquor. At the start of each day the liquor was refiltered, even though no significant precipitation ever occurred. On starting the next run a fresh batch of liquor was obtained. The feed, retentate and permeate liquor samples were analysed for TOC (by OIC analyser), alumina, caustic and soda (by Metrohm titration) and also oxalate (by Dionex IC) for some liquors.

TOC, soda and alumina rejections and in some cases oxalate and Non-Oxalate Organic Carbon (NOOC) rejections were determined using a ratio between the retentate and permeate samples. For example TOC rejection:

1 For this paper, "pure caustic solutions" contain just sodium hydroxide, that is just "free caustic". "Caustic aluminate liquors" contain sodium hydroxide and sodium aluminate (termed "caustic" in the Bayer industry or g/L C as $Na_2CO_3$) and possibly other impurities such as sodium carbonate. Aluminate in these liquors is expressed as g/L $Al_2O_3$. "Soda" as S is the sum of caustic (sodium hydroxide and aluminate) and sodium carbonate.

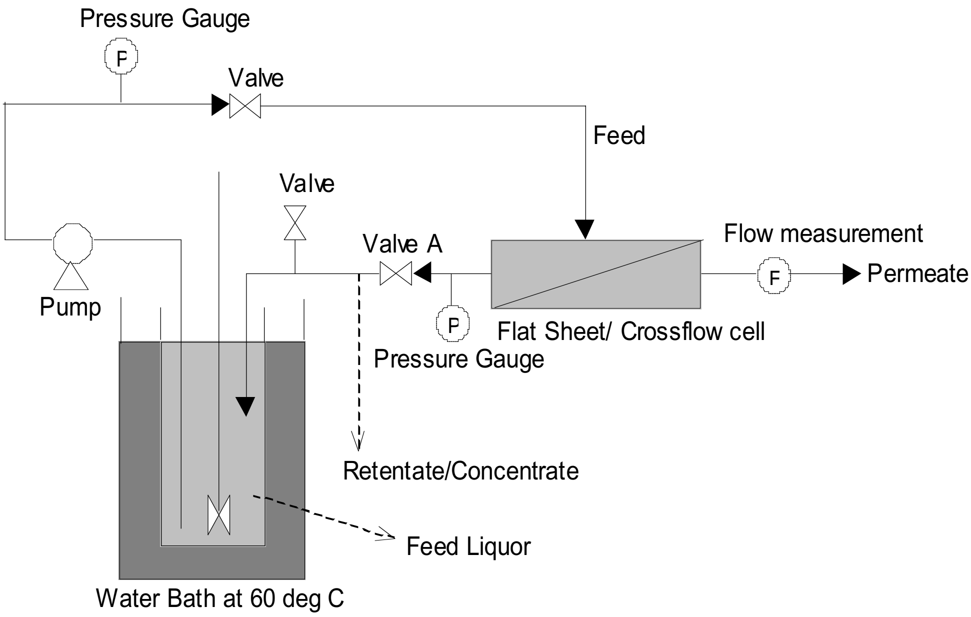


Figure 1 — Flowsheet of the flat sheet membrane test rig.

$$\% \text{ Rejection} = \frac{(\text{Retentate TOC} - \text{Permeate TOC}) \times 100}{\text{Retentate TOC}}$$

(Equation 1)

The permeate flows (mL/s) were converted to a flux (L/m$^2$/hr) using the membrane cross-sectional area, 0.0028m$^2$.

The Coefficient of Variance (CV) for TOC rejection and flux varied from one test to another but gave reasonable results indicating the experimental technique was satisfactory.

## 3. Membrane Performance and Durability — Low Caustic Feed Liquors

The initial set of work to test separation performance with lime treated seed wash filtrate ("LSOF") showed six out of eight membranes were durable in 20g/L free caustic liquor for at least nine weeks, although one of the six (MPF36) gave inconsistent results (Figure 2).

Maximum TOC rejection was 70–75% for MPF34 and 7470. These results show promise for application of NF membranes in an organic removal process, especially since soda recovery (to the permeate) was also high.

Two membranes were removed from testing (NF-70 and DK) because of poor durability in this low caustic concentration.

Testing with seed wash filtrate (B filtrate) showed slight degradation for most membranes after 15–20 weeks (Figure 3).

Best rejection of NOOC ranged from 60–88% for MPF34.[2] Six out of eight membranes still show reasonable rejections (>25%) for NOOC.

Overall fluxes varied quite significantly over the range of membranes, between 15 and 600 L/m$^2$/hr in both LSOF and B filtrate. Storage in caustic generally increased these fluxes but only slightly. Those membranes with higher TOC rejections generally had much lower fluxes, indicating "tighter" porosity. Fluxes were generally higher for LSOF compared with B filtrate.

2 NOOC rather than TOC data are more relevant with seed wash filtrate (B filtrate) as feed, since this liquor has a disproportionately high level of oxalate carbon in its TOC level, compared to base plant liquor.

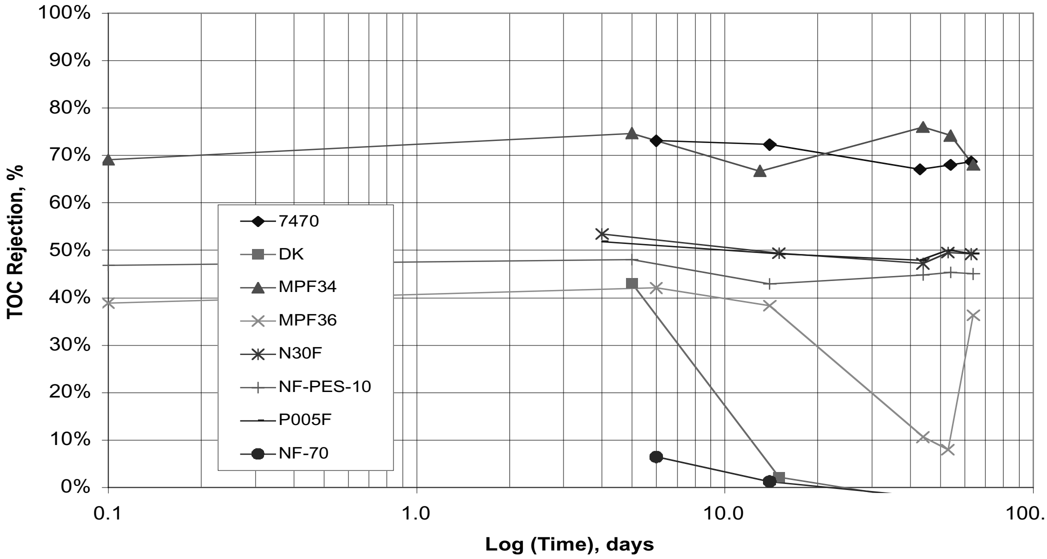


Figure 2: — TOC rejections from a lime treated seed wash feed (LSOF).

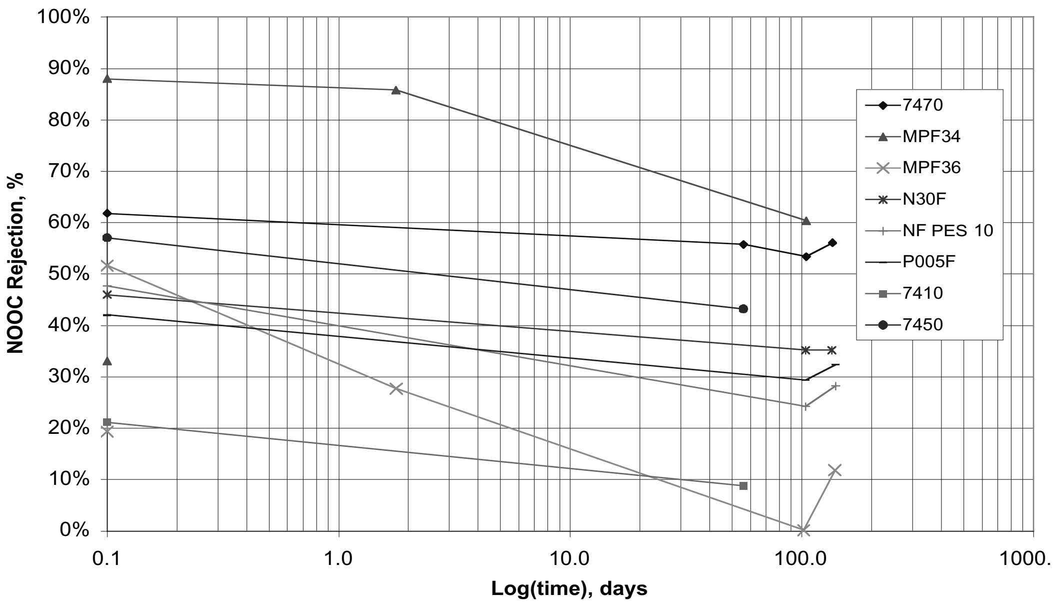


Figure 3: — NOOC rejections from seed wash filtrate feed (B filtrate).

Soda rejections were low for fresh membranes in both LSOF and B filtrate, less than 5% for most cases. For process viability the lower the soda rejection, or more soda permeating, the better. All membranes had low to moderate alumina rejections, generally 6–10%, again the lower the value, the better for process viability.

Oxalate rejection from B filtrate was good for two membranes, 70% for MPF34 and 50% for 7470. The remainder had rejections of less than 30%.

## 4. Membrane Performance and Durability — Medium Caustic Feed Liquors

Maximum TOC rejection from a diluted L-D stream (140g/L C, 82 g/L free caustic) was 30% with fresh membranes ("zero" storage time). Storage in medium caustic aluminate solution (~100g/L C, 80g/L free caustic) over several weeks degraded all membranes to some degree to give a decrease in TOC rejection. Four of the eight membranes tested however had TOC rejections greater than 20% after 11 weeks of storage. These results are illustrated in Figure 4.

Fluxes were lower with diluted L-D than for the LSOF and B filtrate cases, ranging from 6 to 200 L/m$^2$/hr. Storage in caustic increased these fluxes by over 70%. Soda rejections were less than 3% for all membranes and decreased only marginally after storage in caustic. Alumina rejections were also low (<6%). That is, as hoped, most soda and alumina permeate the membranes for recovery to the Bayer process.

## 5. Membrane Performance and Durability — High Caustic Feed Liquors

Test work showed all NF membranes degrade quite rapidly in 270g/L free caustic solution. They showed a marked deterioration in performance for separation of TOC in L-D after a few weeks of contact with caustic solution at 60°C.

Further evaluation this time using a caustic aluminate synthetic liquor with ~180g/L free caustic (265g/L C, 0.295 A/C) for the contact exposure also showed major degradation. After nine weeks contact, TOC rejections had

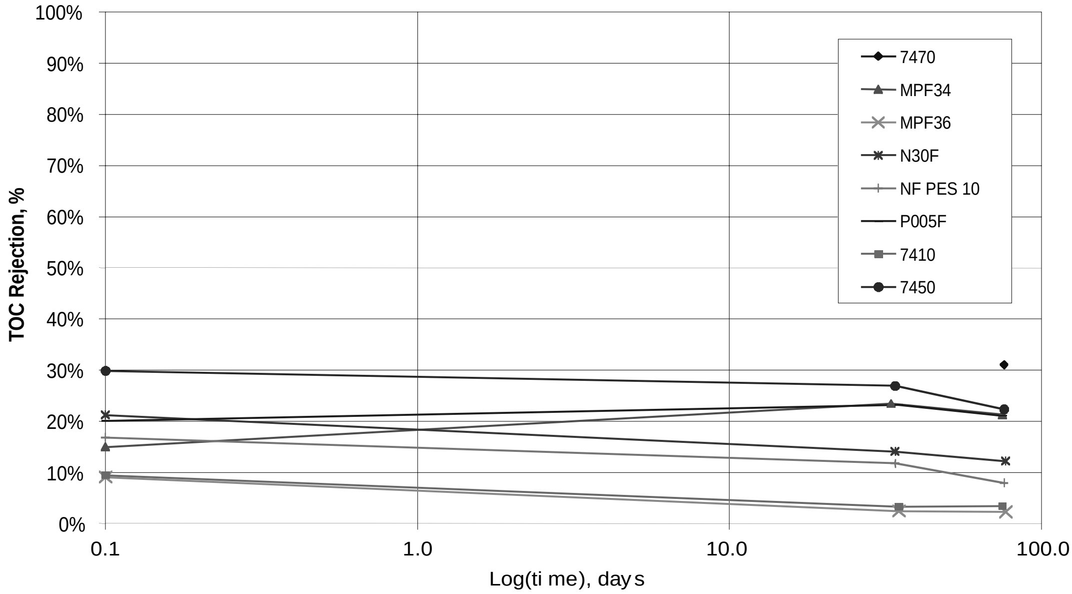


Figure 4 — TOC rejections from a diluted L-D feed after storage in 80g/L free caustic.

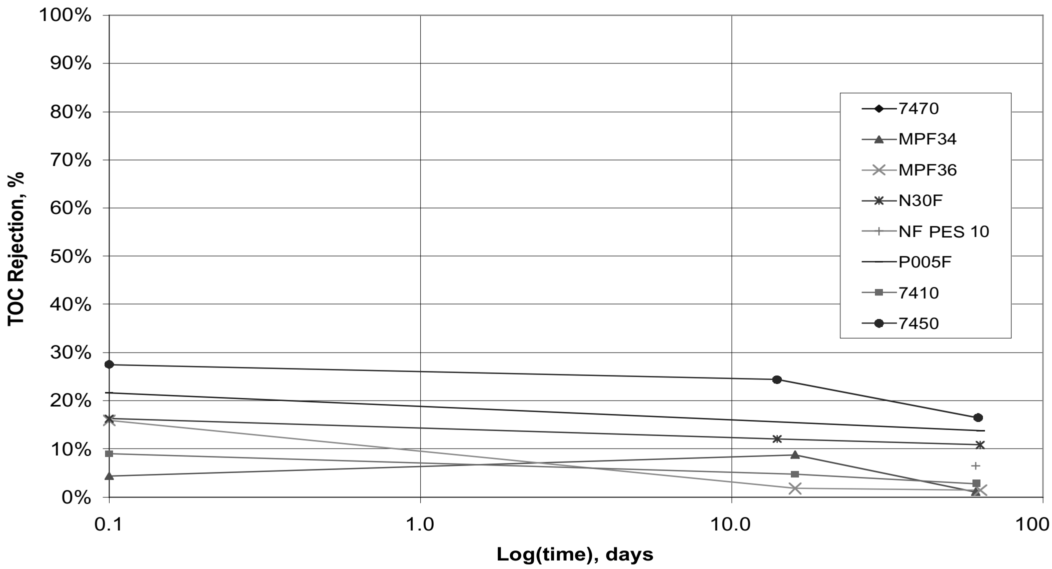


Figure 5 — Repeat TOC rejections from an L-D feed after storage in ~180g/L free caustic solution.

deteriorated in most cases to less than 20%. This is shown in Figure 5.

Fluxes with fresh membranes and L-D feed liquor are very low (1–46 L/m$^2$/hr). After storage in the caustic aluminate synthetic liquor, the fluxes increase in some cases to three times. Soda rejections were low (<5%) and on storage in caustic aluminate liquor, they reduced even further. All membranes had low rejections for aluminate.

## 6. Economic Drivers

The value to the Bayer process of these membranes depends largely on their ability to produce a high impurity concentration in the retentate stream. This in turn is determined by the impurity rejection parameter, particularly the TOC rejection. However, if a high TOC rejection is achieved at the cost of a low membrane flux, capital and operating costs will be high. Low membrane durability in the caustic environment will also increase operating cost.

Thus the ideal membrane is one with high TOC rejection, high flux, and good durability. Membrane flux is probably better expressed as kg soda permeated per m$^2$ per hr, rather than volumetric flux, to reflect the fact that membranes treating a more concentrated feed stream do not have to treat the same volume of feed to deliver the same benefit. Figure 6 shows TOC rejection versus soda flux for all membranes tested, for various feed liquors. It can be clearly seen that LSOF gives the best combinations of flux and rejection, followed by B-Filtrate and then the medium- and high-caustic streams.

Thus, of the feed options explored, treatment of the LSOF or B-Filtrate appear likely to give the best economic return. There is also an accelerated membrane degradation

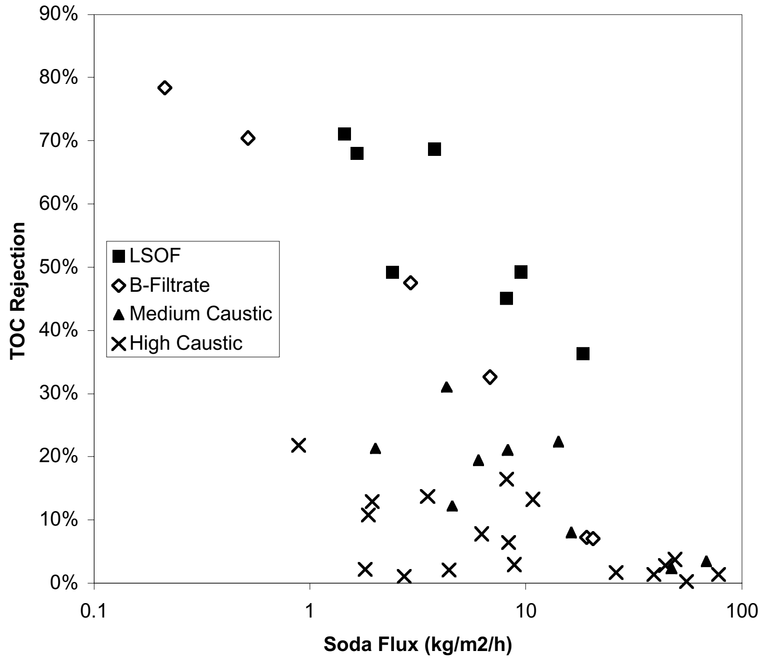


Figure 6 — Membrane TOC rejection as a function of soda **flux.**

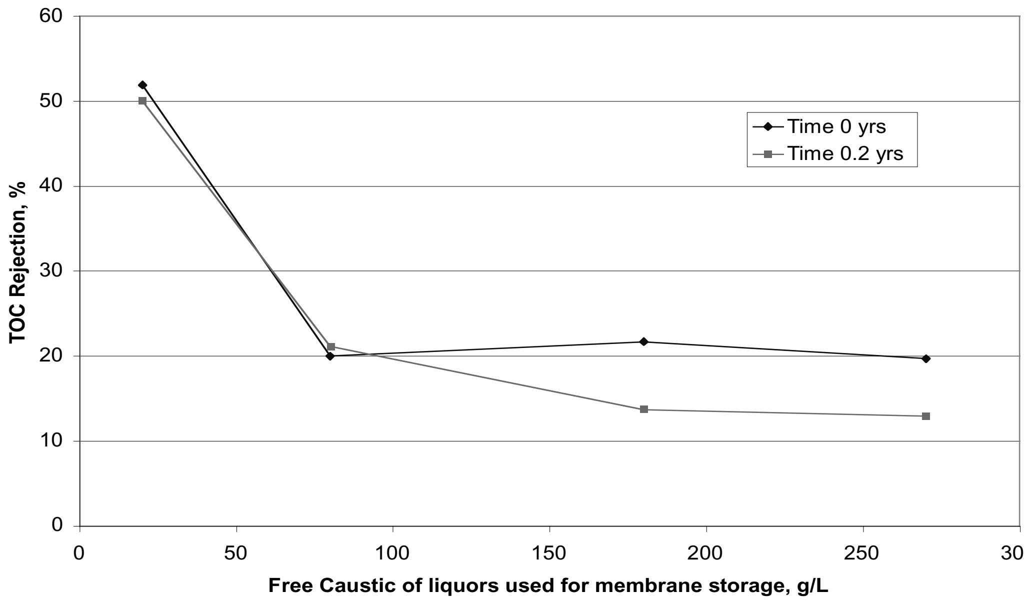


Figure 7 — TOC rejection versus free caustic at zero and 0.2 years storage (for P005F).

in higher free caustic strength liquors, as indicated by the loss of TOC rejection over time in Figure 7.

Thus economic application of these membranes appears limited to fairly dilute caustic streams. This may present problems for handling the retentate stream produced, which will also be quite dilute. Feeding the retentate to a liquor burning process, for example, is probably ruled out by the need for an additional evaporation step. More attractive processing options at low caustic concentrations include wet oxidation, biological degradation, and disposal with mud residue.

Figure 7 also shows that at lower caustics there is a much greater rejection of organics. Or put another way, more organics are passing through the membrane (in permeate) at higher caustics. This phenomenon indicates that the ionic strength or alkalinity of the feed is impacting the membrane separation performance. That is rather than a simple separation according to molecular weight, the degree of ion-pairing and the ionic transport behaviour may be important particularly at the charged surface of the membrane. A contributing factor may also be some physical modification of the membrane porosity to allow a higher permeation of organics (ie lower rejection) at higher caustic strength solution.

## 7. Conclusions

The durability and separation performance of NF membranes have been tested for potential applications in a Bayer refinery for soda recovery and organics disposal. Six nano-filtration membranes demonstrate durability in low and medium caustic liquors (at least up to 82g/L free caustic) as flat-sheet configurations. However, all membranes tested in high free caustic liquors (>184 g/L free caustic) were not durable and degraded over a relatively short period of time.

Membrane operation at low to medium free caustic feed levels appears most likely to give economic return. The possible scenarios for such a process are outlined in a recent patent application. (Armstrong et al, 2000)

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