NanoPro® AS-3012

Performance Report

Content

1. Material and Methods

1.1 Experimental Set-up

The screening of the 33cm^2 piece membrane samples has been conducted with a crossflow labscale filtration system.

1.2 Membrane Samples

The membrane samples have been punched to rectangle pieces of 33cm^2 and washed using the above described filtration system for about 10 hours (overnight) in RO water of 13 µS/cm at 25°C electrical conductivity, that has been manufactured using a RO membrane device.

1.3 Investigated Parameters

The experiments were conducted at 40 bar, a constant feed flow rate of about 80l/h and at a temperature of (30 ± 1) °C unless stated otherwise. Permeate flux JP has been calculated by time t necessary to collect a permeate sample of volume V relative to membrane filtration area A of 33cm^2, from each cell at each pressure applied.

$$J_p = \frac{V}{t \cdot A} \qquad (1)$$

Observed rejection R for selectivity of $MgSO_4$ at 40bar and NaCl at increasing pressure was calculated using electrical conductivity ratios as suggested in the following equation:

$$R = 1 - \frac{k_{25}^{p}}{k_{25}^{f}} \qquad (2)$$

Where k^{p}_{25} and k^{f}_{25} are the electrical conductivity of permeate and feed at 25 °C, respectively [2].

1.4 Sampling and Analytics

Each sampling covered a permeate sample from each membrane cell and a feed sample directly taken from the feed tank. Samples were taken after one hour of circulation in the flat membrane system (described above) at each testing pressure.

2. Results

2.1 Chemical Stability

2.1.1 Solvent Stability

The membranes were immersed in pure organic solvents *(NMP, Acetonitrile, Ethyl acetate, Toluene, THF, 2-Propanol) for a period of 2 months at 25^{0}C.*

The flux and rejection were conducted at 40 bar with pure water for flux measurements and 5% Glucose for rejection. The results of ROW flux and Glucose rejections are shown in table 1.

Initial performance: Flux: 2909 LMD and Glu. Rejection: 97.5%.

No degradation in performance has been observed after 2 months immersion in the reported solvents.

It is important to note the exceptional stability in polar a-protic solvents. Such stability in these conditions is unprecedented in commercial NF membranes.

Table 1: Chemical stability -ROW Flux & Glucose Rejection after 2 month immersion in organic solvents

Solvent	Flux [LMD]	Glucose rejection [%]
Acetonitrile	1818	98.5%
Ethyl acetate	2618	97.4%
2-Propanol	1527	97%
THF	1964	97.6%
Toluene	1818	98.2%
NMP	1891	98 %

2.1.2 Stability in Hot Acid and Solvent

The membranes were immersed in pure *NMP* and in a *10% NMP:10% H_2SO_4 mixture at 60^0C for 300 hrs* (which equals to 4800hrs in 20°C). Another membrane was immersed in 20% H_2SO_4 at 90^0C for 300hrs (which equals to 38,400hrs = 4 years & 4 months in 20°C).

The flux and rejection were conducted at 40 bar with pure water for flux measurements and 5% Glucose for rejection.

The results of ROW flux and Glucose rejections are shown in table 2.

<u>Initial performance:</u> Flux: 2850 LMD and Glu. Rejection: 97%.

The performance of the membrane under these extreme conditions is highly impressive. No degradation in performance is observed.

NMP is considered to be a very aggressive solvent even at RT. A mixture of NMP and acid at elevated temperatures does not affect the membrane performance. The hot acid stability of the membrane is the best in the membrane world today. It is **the only membrane** in **the world** that the combination of acid and solvent does not affect its performance for a long period of time.

Table 2: Chemical stability -ROW Flux & Glucose Rejection after immersion in hot NMP/Acid

Immersion liquid composition	Temperature [^oC]	Time [hrs]	Glucose Rejection [%]	Flux [LMD]
100% NMP	60	24	98	2850
		100	95	3600
		300	91	3300
10%NMP 10% H_2SO_4	60	24	95	2700
		100	97	3300
		300	96	3300
20% H_2SO_4	90	24	97	2850
		100	97	3600
		300	97	3000

2.1.3 Pure Water Flux and Permeability

The results of pure water flux and permeability are shown in table 3 and figure 1. The increase in pressure leads to an increase in flux and permeability. This increase is almost linear and therefore predictable by a simple equation.

Table 3: Flux / Permeability versus Pressure

Pressure (bar)	Flux (LMH)/(LMD)	Permeability (L/m^2hrbar)
4	13.0 / 312.0	3.3
10	35.5 / 852.0	3.6
20	76.4 / 1833.6	3.9
30	121.1 / 2906.0	4.0
40	170.8 / 4099.2	4.3

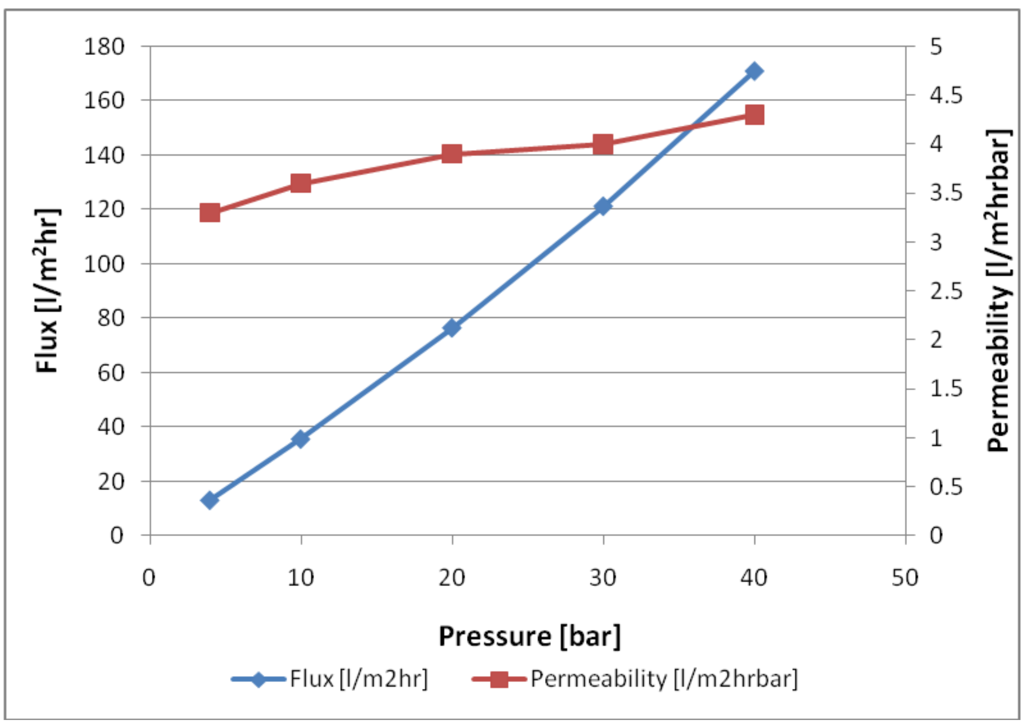


Fig. 1: Pure water Flux & Permeability

Experiments have been performed at (30 ± 1) °C and feed pressures as stated in table 3. All data points represent an average value of six measurements from each cell, of pure water flux (blue) and permeability (red).

2.1.4 Rejection of $MgSO_4$

The results of rejection tests of $MgSO_4$ solution are shown in table 4 and fig.2. The divalent salt rejection rises with pressure, reaching an apparent plateau at a pressure of roughly 40 bars. This phenomenon also demonstrates the effect of membrane compaction, although it is minor.

Table 4: Rejection versus Pressure

Pressure]bar]	Rejection [%]
4	95.4
10	96.4
20	97.0
30	97.4
40	**97.5**

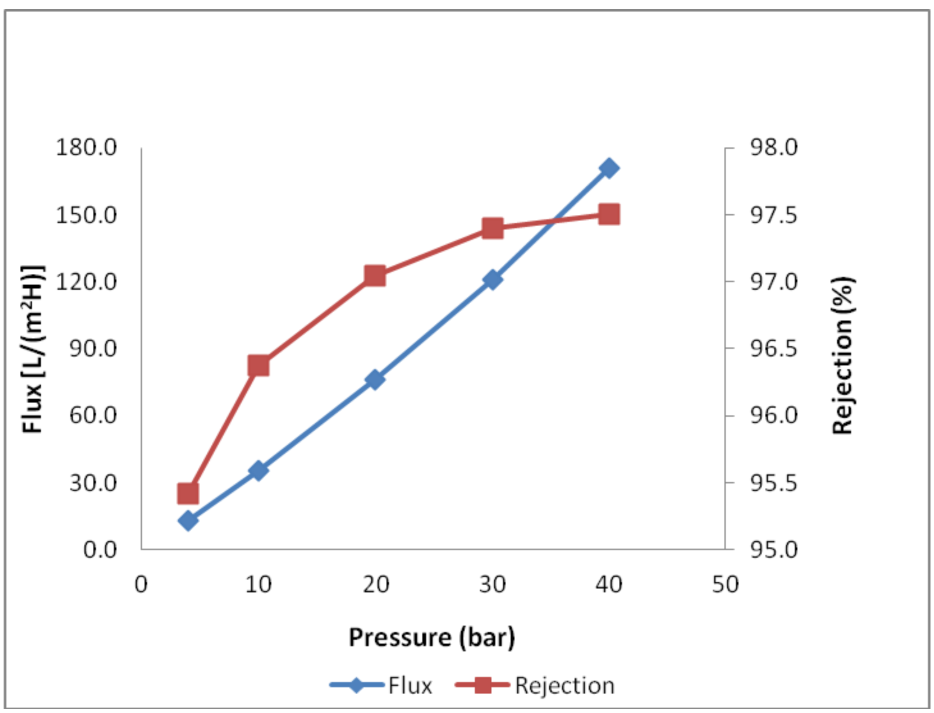


Fig. 2: Pure water Flux and Rejection of magnesium sulfate

Experiments have been performed at (30 ± 1) °C and feed pressures as stated in table 4.
All data points represent an average value of six measurements from each cell (the system described above), of pure water flux (blue) and rejection (red) of 2000ppm $MgSO_4$ solution

2.1.5 Hysteresis – Compaction Displacement

2.1.5.1 Flux/Permeability

The results of flux and permeability as function of pressure (increasing and decreasing) are summarized in table 5 and figures 3 & 4. It can be observed that the membrane shows elasticity at pressures above 20 bar – the values for flux and permeability are practically the same with rising and decreasing pressures. The minor increase observed in the permeability while decreasing the pressure can be referred to the wetting of micro-pores at high pressure values and thus, increasing the membrane flux potential at lower pressure values.

Table 5: flux & permeability as function of pressure

Pressure	Flux (P increasing) [LMD]	Flux (P decreasing) [LMD]	Permeability (increasing)	Permeability (Decreasing)
10	387	537	1.6	2.2
20	1050	1219	2.2	2.5
30	1860	1848	2.6	2.6
40	2628	2800	2.7	2.9
53	3441	3628	2.7	2.9
60	4000	4073	2.8	2.8
65	4339		2.8	

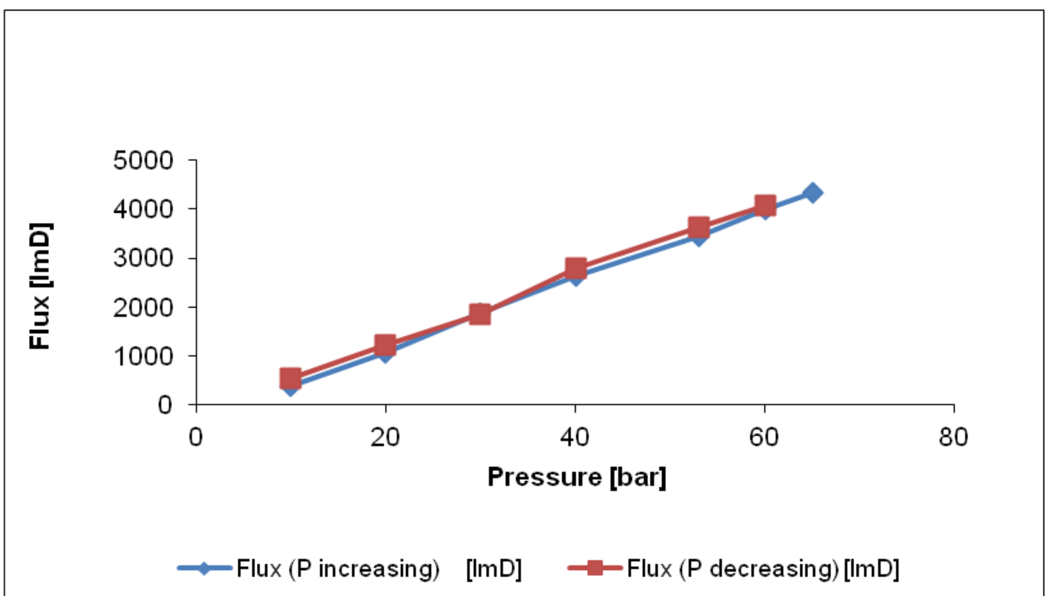


Fig. 3: Flux as function of pressure

Experiments have been performed at increasing pressure followed by decreasing pressure as stated in the graph Feed temperature of (30 ± 1) °C and a constant feed flow rate of about 80l/h. All data points represent average values.

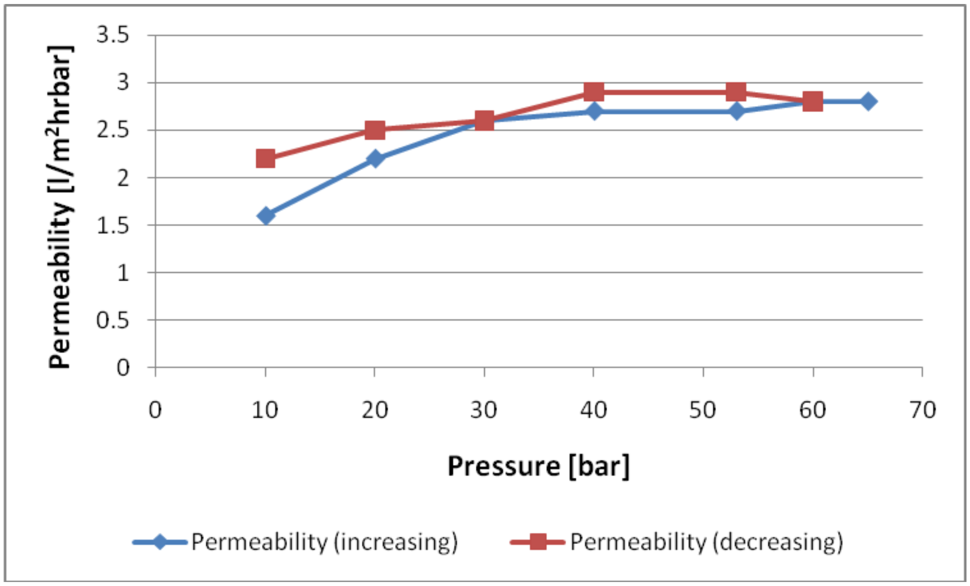


Fig. 4: Permeability as function of pressure

Experiments have been performed at increasing pressure followed by decreasing pressure as stated in the graph Feed temperature of (30 ± 1) °C and a constant feed flow rate of about 80l/h. All data points represent average values.

2.1.5.2 $MgSO_4$ Rejection

The results of magnesium sulfate rejection as function of pressure (increasing and decreasing) are shown in table 6 and figure 5. Again it is observed that at pressures exceeding 20 bar, the membrane stabilizes and shows practically no dependence of divalent cation rejection on pressure.

Table 6: $MgSO_4$ rejection as function of pressure

pressure [bar]	Rejection [%] - Pressure increasing	Rejection [%] - pressure decreasing
10.0	94.6	98.4
20.0	98.2	92.5
30.0	98.7	98.8
40.0	98.8	98.9
50.0	99.0	99.0
60.0	99.0	99.0
65.0	99.1	99.1

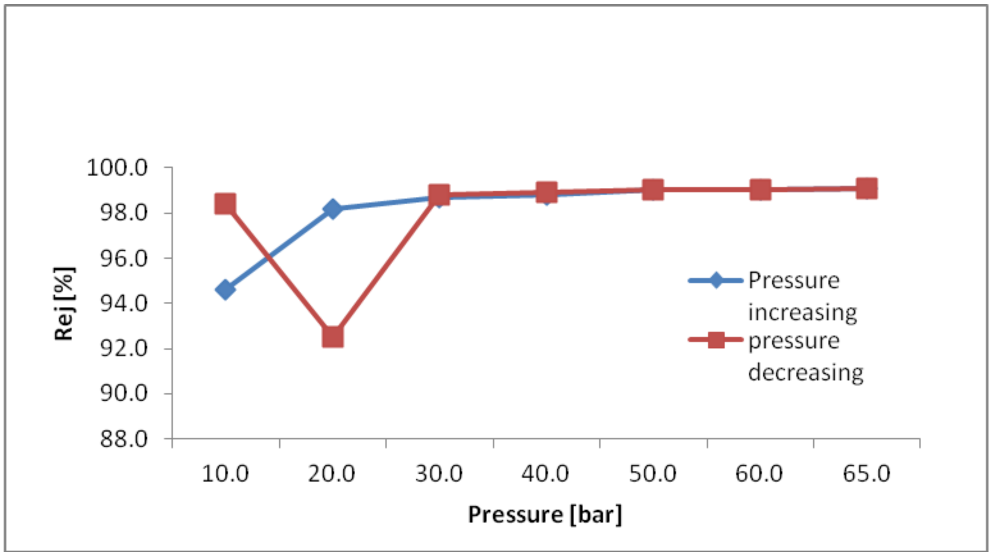


Fig. 5: $MgSO_4$ Rejection as function of pressure

Experiments have been performed at increasing pressure followed by decreasing pressure as stated in the graph feed temperature of (30 ± 1) °C and a constant feed flow rate of about 80l/h. All data points represent an average values.

2.1.5.3 Glucose Rejection

The results of Glucose rejection as function of pressure (increasing and decreasing) are shown in table 7 and figure 6. The effect of pressure on glucose rejection is within experimental error.

Table 7: Glucose rejection as function of pressure

pressure [bar]	Rejection [%] - Pressure increasing	Rejection [%] - Pressure decreasing
10.0	96.8	96.1
20.0	96.9	96.1
30.0	97.4	96.6
40.0	97.3	97.2
50.0	97.2	97.1
60.0	97.8	97.2
65.0	97.3	97.3

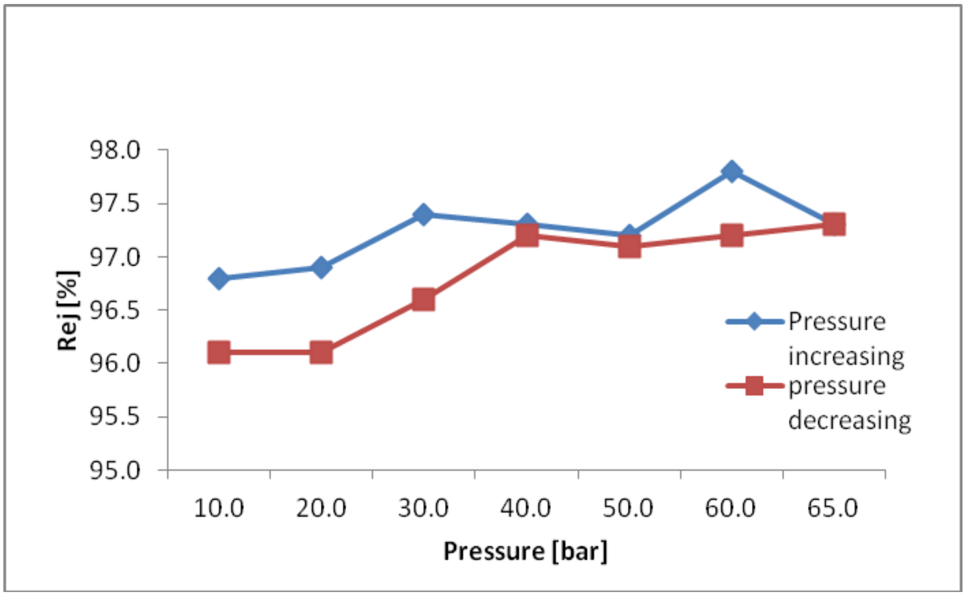


Fig. 6: Glucose Rejection as function of pressure

Experiments have been performed at increasing pressure followed by decreasing pressure as stated in the graph feed temp of (30 ± 1) °C and a constant feed flow rate of about 80l/h. All data points represent an average values.

2.3 Flux Dependence on pH

The results of flux measurements as a function of the pH are shown in table 8 and figure 7.

The flux generally drops as pH rises. Due to the amphoteric nature of the membrane acidic environment increases the hydrophilicity of the membrane, thus increasing flux at pH 1 by 60% over the flux at neutral pH. The flux is practically constant between pH 4 and 12.

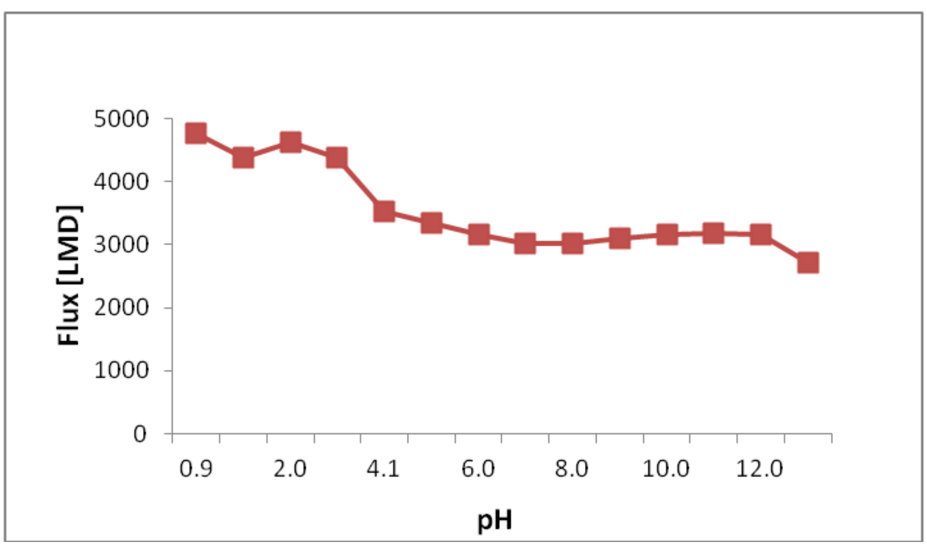


Fig. 7: Flux as function of pH

Experiments have been performed at 40bar, feed temperature of (30 ± 1) °C and feed pH as stated in the graph. All data points represent an average value of six measurements from each cell (the system described above).

Table 8: flux & permeability as function of pH

pH	Flux [LMD]	permeability
0.85	4771	5.0
1.02	4375	4.6
1.99	4622	4.8
2.99	4371	4.6
4.07	3522	3.7
5.06	3348	3.5
6.00	3170	3.3
7.00	3019	3.1
8.01	3019	3.1
9.08	3098	3.2
10.00	3161	3.3
11.00	3180	3.3
12.00	3170	3.3
13.00	2722	2.8

2.4 Acidic Streams

2.4.1 Acid Rejection

The feed chamber was filled with an acid solution of varying concentrations of sulfuric acid. The flux and rejection were measured at 40 bar and at 70 bar. The results of flux and acid rejection are shown in table 9.

Table 9: Acid rejection and flux/permeability data

	40bar			70 bar		
H_2SO_4 [%]	Flux [lmd]	permeability [lmh/bar]	Acid rejection [%]	flux [lmd]	permeability [lmh/bar]	Acid rejection [%]
1	1800	1.88	12.5	2909	1.73	12.5
10	1309	1.36	12.5	2127	1.27	17.5
15	909	0.95	13.3	1637	0.97	12.0
20	776	0.81	6.4	1382	0.82	8.3
25	630	0.66	4.7	935	0.56	6.3

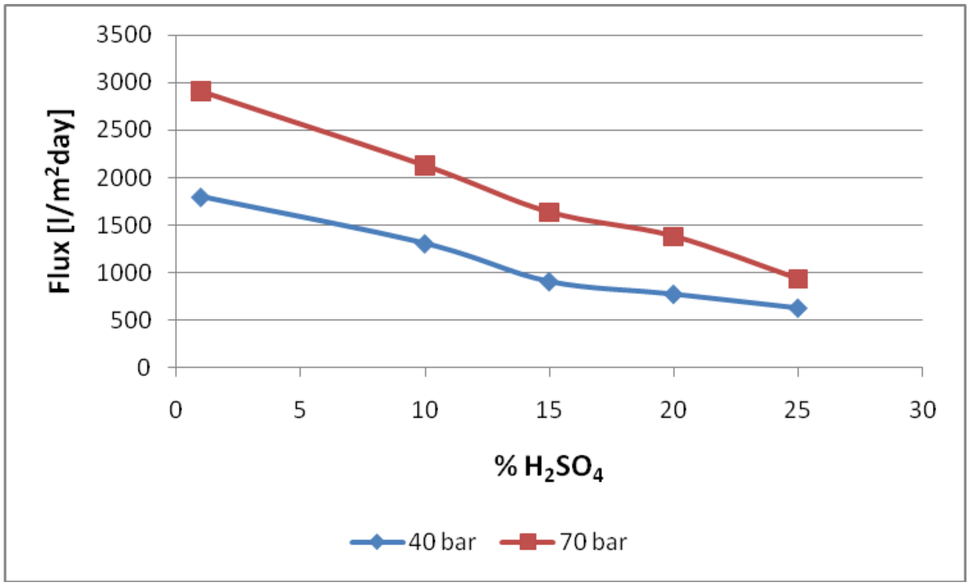
2.4.2 Flux and Permeability as a Function of Acid Content

The results of flux and permeability are shown in table 10 and figure 8. According to these, flux and permeability decrease with the added acid concentration, probably because of the combination of increased viscosity and slightly due to osmotic pressure. The permeability is practically independent of operating pressure between 40bar and 70bar. This leads to the conclusion that osmotic pressure plays a small role in the loss of flux with increased acid content. The conclusion is further supported by the low acid rejection observed.

Table 10: Flux / Permeability versus acid content at 40 bar & 70 bar

	40 bar		**70 bar**	
[%] H_2SO_4	**Flux [lmd]**	**permeability [lmh/bar]**	**Flux [lmd]**	**permeability [lmh/bar]**
1	1800	1.88	2909	1.73
10	1309	1.36	2127	1.27
15	909	0.95	1637	0.97
20	776	0.81	1382	0.82
25	630	0.66	935	0.56

A



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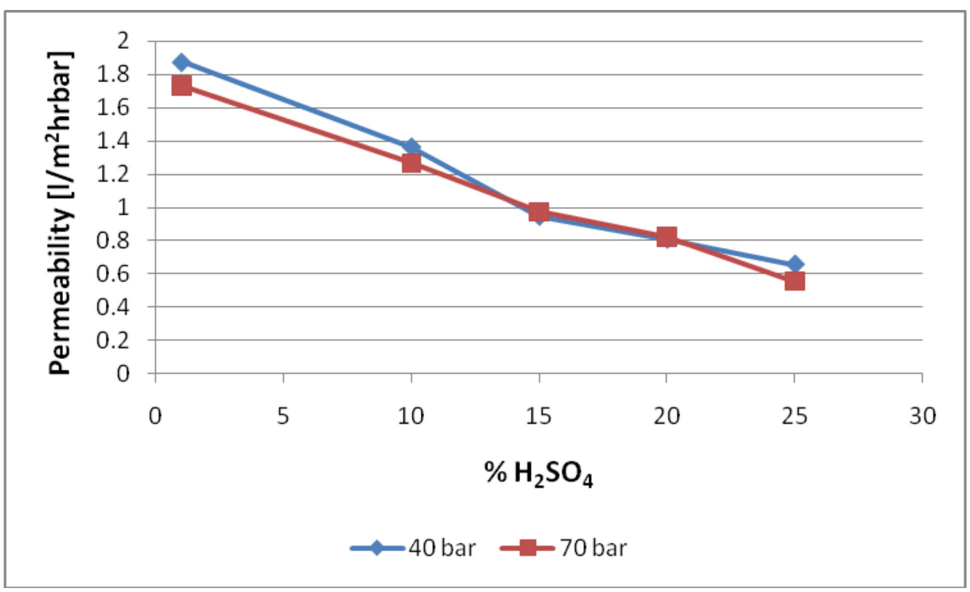

Fig. 8: Flux (A) and permeability (B) as function of acid content at 40 and 70 bar.

2.4.3 Acid Rejection as a Function of Acid Content

The results of rejection tests of H_2SO_4 are shown in table 11 and fig.9. It can be seen that the ***rejection decreases*** from 12.5% to ~5% ***with climbing acid content*** and is slightly higher at 70 bar than at 40 bar. It is suggested that the higher rejection stems from the higher flux through the membrane.

Table 11: Acid rejection versus acid content

	40bar	**70 bar**
[%] H_2SO_4	**Acid rejection [%]**	**Acid rejection [%]**
1	12.5	12.5
10	12.5	17.5
15	13.3	12.0
20	6.4	8.3
25	4.7	6.3

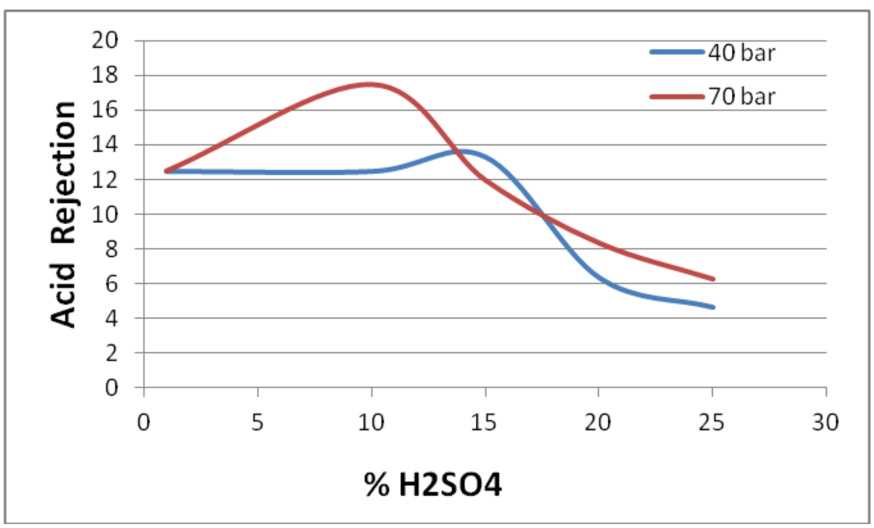

Fig. 10: Acid rejection as a function of acid content

2.4.4 Glucose Rejection in Acidic Streams

The results of the glucose rejection measurements are summarized in table 12. Measurements were conducted by measuring the TOC of the concentrate and permeate. An attempt was made at measuring the index of refraction (Brix), however, the results of this experiment were obscured by the index of refraction of the acid in the stream.

Table 12: Glucose rejection versus acid content

	Glucose rejection	
[%] H_2SO_4	**40 bar**	**70 bar**
10	96	95.8
15	95.3	96.1
20	94	93.8
25	94.2	94.7

A slight decrease in glucose rejection is observed. This decrease can probably be attributed to the decrease in flux that takes place at higher acid concentrations.

Membrane AS-3012 (1530) was analyzed for acid and glucose rejection at different sulfuric acid concentrations and operating pressures. With higher acid concentrations, the viscosity rose, thereby bringing a decrease in flux and permeability. The lower flux, in turn, gives higher acid rejection and slightly lowers the glucose rejection.

There is practically no difference in permeability between the two work pressures used, 40 and 70 bar. Thus, the flux at 70 bar is higher than 40 bar. This leads to a higher acid rejection at 70 bar. It was expected to increase the acid rejection. However, if such an increase took place, it was below the noise level of the experiment.

2.4.5 Ion Rejection at Acidic pH

The membrane rejection to different divalent and trivalent ions was measured at pH=1 with 30 bars of pressure. The membrane rejects more than 96% of all ions measured. Results are summarized in table 13.

The amphoteric nature of the membrane, and as an outcome its high charge at pH=1 as shown by its high flux in p.2.3 supports this behavior

Table 13: Rejection of different ions

Ion	Rejection
SO_4^{2-}	96%
Al^{3+}	100%
Fe^{3+}	99%
Cu^{2+}	96%
Ca^{2+}	97%
Mg^{2+}	99%
Mn^{2+}	98%

2.5 Performance Dependence on Temperature

Flux (figure 11) and rejection (figure 12) were measured at various temperatures to establish the temperature dependent behavior of the membrane. As the temperature rises from RT to 70^{o}C, an increase of two-fold ($\times$2) is observed in flux. Another measurement (not shown in the figures) of the membrane characteristics at RT after the system has cooled down to 30^{o}C shows that the membrane relaxes back to initial performance. Glucose rejection drops by 4% from RT to 70^{o}C and magnesium sulfate rejection drops by 2.5% over the same range. A measurement the membrane characteristics after the system has cooled down to 30^{o}C (flux 2900 lmd, Mg rejection 96.7% and glucose rejection 99.1%) shows that the membrane relaxes back to initial performance (flux 2900 lmd, Mg rejection 96.9% and glucose rejection 99.9%) .

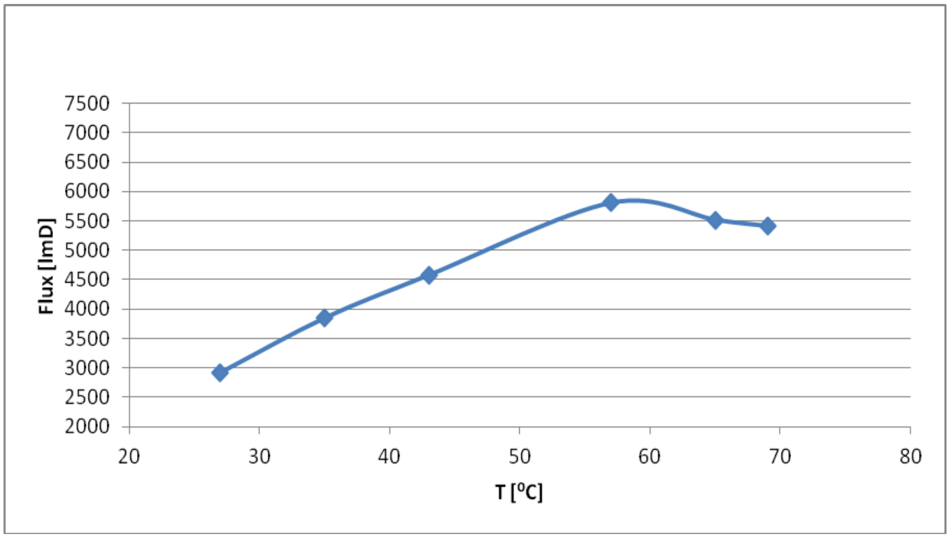

Fig. 11: Flux as function of temperature
Experiments have been performed at 40bar, feed temperature as stated in the graph.
All data points represent an average value of six measurements from each cell (the system described above).

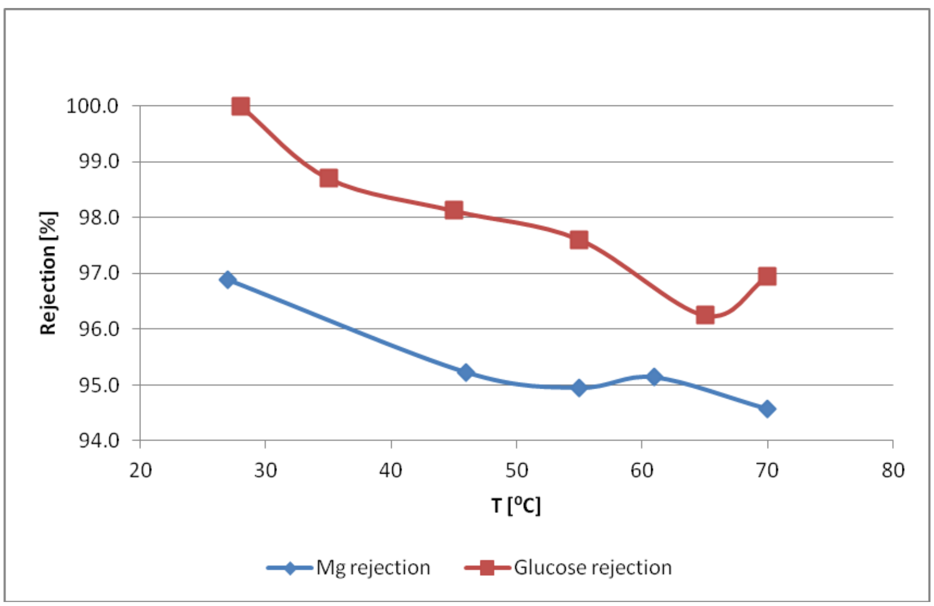

Fig. 12: Glucose and magnesium sulfate rejection as function of temperature
Experiments have been performed at 40bar, feed temperature as stated in the graph. All data points represent an average value of six measurements from each cell (the system described above). Magnesium data was collected after a heating – cooling cycle in ROW. Glucose data was taken after a heating cycle with ROW, followed by a heating cycle with $MgSO_4$ solution and a thorough ROW rinse.