Mine Water Treatment by Membrane Filtration Processes – Upscale Experiments

Nanofiltration, reverse osmosis, mine water, scaling, atomic force microscopy

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The worlds' diminishing water resources together with stricter environmental legislation lead to the development of new technologies for the treatment of water for mining activities. In arid and remote mining areas a promising approach is the integration of membrane technology into state of the art mine water treatment processes. Reverse Osmosis (RO) as well as the lower pressure nanofiltration (NF) may be suitable operations to be considered. Recently an NF membrane identified in previous tests was subject to further investigation in two upscale modules. The acidic water, containing sulphate and a variety of metals, was fed into a disc- and a Spacer Tube® spiral wound module in recycle mode. The setup was tested at different working points over 145 h for each run. The results show applicability of NF for desalination of AMD under the mentioned conditions. No visible drop in permeate flux was observed, although some scaling occurred.

1. Introduction

Stricter environmental legislation, together with the worlds' diminishing water resources lead to the development of new technologies for the treatment of water from mining activities. In arid and remote mining areas a promising approach is the integration of membrane technology into state-of-the-art mine water treatment processes. The proven reverse osmosis (RO) as well as the lower pressure nanofiltration (NF) may be suitable operations to be considered. In previous experiments, several reverse osmosis and nanofiltration membranes were screened with reference water of low pH and with high sulphate and metal content to identify a suitable membrane with satisfactory multivalent ion-retention and flux.

To make a statement on the long-time-performance of the membranes under practical conditions, one of the screened membranes, NF99 of Alfa Laval Mid Europe GmbH, was fitted into a disc module MD 12 of EnviroChemie GmbH, Germany, and a Spacer Tube® module of Rochem RO-Wasserbehandlung GmbH, Germany. As in the previous screening, experiments of about 145 h were conducted at different process parameters such as feed temperature, pressure, flowrate and concentration. A big concern regarding membrane operation in water and wastewater treatment is inorganic fouling, also known as scaling, which occurs depending on the "[…] operation parameters (such as shear rate, and operating pressure) and membrane properties (e.g. porosity, roughness, etc.). […]" [8]. While the operation parameters influence the concentration polarisation near the membrane surface, the low pH can even alter the membrane properties over time. This results in a change in retention or flux [9]. There are studies dealing with the membrane behaviour in the treatment of low pH water, though the membranes are usually tested for systems with few components [9, 2]. In this study a more complex model water, containing aluminium, calcium, magnesium, manganese, copper, iron and sulphate was examined. The flux over time at different operation parameters was recorded to possibly detect a drop in flux which could be an indicator for scaling. To detect modifications of the membrane surface, samples of membrane pockets, which stayed in the module over the whole time of the experiments, were scanned with atomic force microscopy. AFM is often used to characterize the membrane surface, e.g. to calculate the roughness of the surface, which can allow an evaluation of the probability of scaling on the membrane [1, 5].

2. Methods

2.1 Experimental setup (*Figure 1*)

The experiments were conducted with a membrane test rack of Sempas Membrantechnik GmbH, Germany, which is originally equipped with two membrane test cells for testing 90 mm diameter circular membrane patches. The setup was modified to host a disc module MD 12 of EnviroChemie GmbH, Germany, and a Spacer

Tube® module of Rochem RO-Wasserbehandlung GmbH, Germany. These were equipped with the NF99 (now NF only) nanofiltration membrane of Alfa Laval Mid Europe GmbH, Germany, which is a thin film composite membrane with an active polyamide separation layer. Every second space in the disc module out of 160 for a membrane patch was occupied, resulting in a total area of 6.00 m^2. The Spacer Tube® module has about 7.43 m^2 of active membrane surface. The setup comprises a 30 L feed tank and a Cat Pump 1051 plunger pump of Cat Pumps Deutschland GmbH, Germany.

2.2 Pure water flux

The pure water flux was tested with water, deionised by reverse osmosis down to an electrical conductivity of 35 to 40 µS/cm at a temperature of 25 °C. Between each run of the 145 h experiment the clean water conductivity was measured. The membrane was rinsed with pure water and a flow of about 800 L/h was set up to go through the module. The pure water flux was measured at different pressures after reaching a constant flux. In the beginning of the experiments, the watered membranes were even conditioned with pure water over about 1 h at a pressure of 20 bar.

2.3 Model water

The long-time performance of the membrane was tested with a model water of equal ion composition as mine water obtained from a copper mine in Chile with a low pH and high sulphate content. After mixing and dissolution of chemicals, the remaining solid particles, probably Goethite, were removed with a Filtrak 388 filter paper from Munktell & Filtrak GmbH, Germany. Small amounts of H_2SO_4 were added to reach a pH of 2.4. The composition according to a model water analysis for normal model water with the composition most similar to the original water and the concentrated model water used can be found in **Table 1**.

2.4 Procedure

Directly after measuring the clean water flux, the experiments were run over about 145 h, each at different pressures and two different concentrations of the model water. An overview can be found in **Table 2**. Once set up, the parameters were kept constant during the duration of the experiment. The flow of feed, concentrate and permeate was read in regular intervals and the electrical conductivity and the pH-value were measured. Samples of each run were stored for ion analysis in standard polypropylene sample tubes. The electrical conductivity was measured with a WTW Cond 340i conductivity meter and the pH was measured with a WTW pH340 pH-Meter of *Wissenschaftlich-Technische Werkstätten GmbH, Germany*. The flow of the concentrate was read from a mechanical flow meter connected to the SEMPAS test rack whereas the permeate flow was meas-

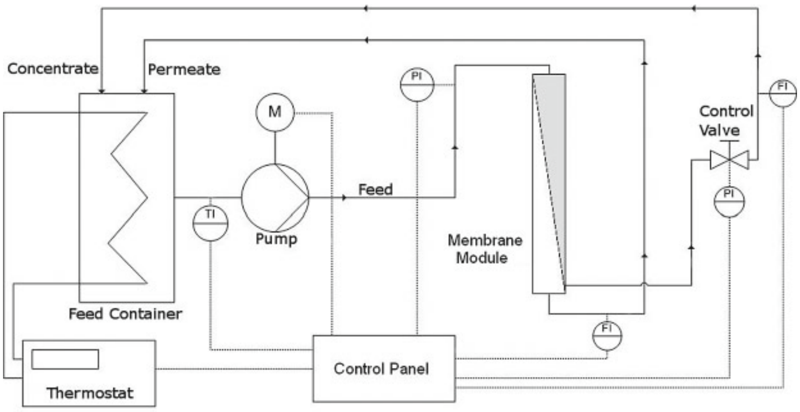

Figure 1*. Flow sheet of the membrane test rack used in the experiments.*

Table 1. Analysis for the model water in original condition and concentrated.

	Original model water (experiment no. 2)		**Concentrated model water (experiment no. 5)**	
	concentrate	**feed**	**concentrate**	**feed**
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Sulphate	21,350	16,542	32,350	30,820
Copper	4,182	3,077	4,988	4,698
Iron	1,247	911	1,435	1,338
Manganese	400	293	477	446
Calcium	566	415	579	545
Magnesium	1,168	857	1,463	1,350
Aluminium	1,937	1,412	2,378	2,203
Conductivity (mS/cm)	15.8	13.1	19.5	19.1
pH-value	2.4	2.4	2.4	2.4
Temp. (°C)	20	20	20	20
Saturation index (PhreeqC)				
Copper ferrite ($CuFe_2O_4$)	2.78	2.41	2.42	2.32
Goethite (FeO(OH))	3.96	3.84	3.78	3.75
Gypsum ($CaSO_4$)	0.08	–0.05	0.21	0.19

Table 2. Overview schedule of experiments.

Long-time experiment no.	**Water**	**Module**	**Parameter**	
			Flow (L/h)	**Pressure (bar)**
1	normal concentration	Disc	1000	5
2	normal concentration	Disc	1000	20
3	normal concentration	Disc	500	5
4	normal concentration	Disc	500	20
5	double concentration	Disc	1000	5
6	double concentration	Disc	1000	20
7	double concentration	Disc	500	5
8	double concentration	Disc	500	2
9	normal concentration	ST®	1000	5
10	normal concentration	ST®	1000	20

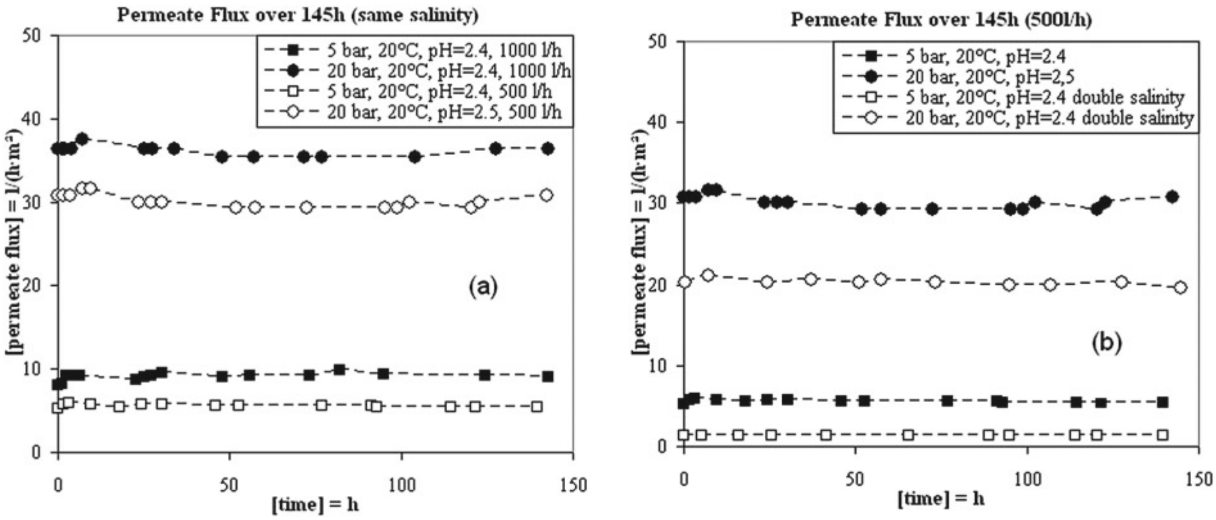

Figure 2. *Permeate flux over time for (a) constant salinity, two different feed flows of 1000 l/h and 500 l/h and two different pressures of 5 bar and 20 bar and (b) constant feed flow of 500 l/h and two different feed concentrations with high and low salinity as specified in* ***Table 1*** *and two different pressures of 5 bar and 20 bar.*

ured manually with a 2 L graduated cylinder and an electronic time clock. The concentrate and permeate were recycled to the feed tank.

The analysis of the cations aluminium, calcium, magnesium, manganese, copper and iron was done with an Optima 3000 ICP-EOS of Perkin-Elmer, USA. Sulphate as the only anion in the model solution was analysed with a sulphate cuvette test LCK 353 of Hach-Lange GmbH, Germany.

2.5 Atomic force microscopy

Atomic force microscopy seems to be a suitable tool to characterize the properties of the membrane structure [1]. In this study two membrane samples from the disc module MD 12 were taken at different times of the total time of the experiments. The visualisation of the surface with an atomic force microscope XE-100 of Park Systems, USA, equipped with an ACTA cantilever of AppNano, USA, in non-contact mode, was tried to detect changes in the membrane surface and structure.sTo this end, patches of 10 x 10 mm of the deionised water rinsed membrane were prepared for analysis after each 145 h run of the experiment.

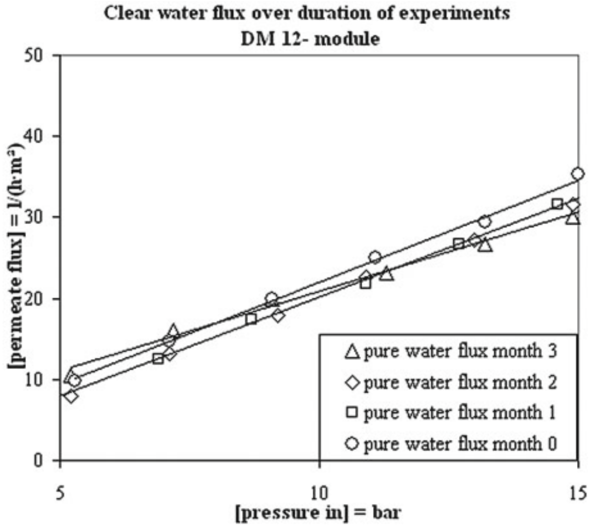

Figure 3. Clear water flux at different times of experiment from the beginning (0 months) to the end after 3 month.

3. Results and Discussion

3.1 Disc Module

Figure 2 shows the flux of the MD 12 module over a time of 145 h. In **Figure 2 (a)** the flux at different feed flow rates and pressures is compared. The graphs with filled outline show the flux at a feed flow rate of 1000 l/h whereas the graph with unfilled outline represents the flux at a feed flow rate of 500 L/h. For each feed flow rate a pressure of 5 bar as well as 20 bar was investigated. **Figure 2 (b)** shows the permeate flux over time for a constant feed flow rate of 500 l/h at 5 bar and 20 bar and with two different concentrations of the feed.

It can benseen from **Figure 2 (a)** that the flux is almost four times higher at 20 bar compared to 5 bar, as expected from the near linear relationship between pressure and flux (below critical flux). When Comparing the two feed flow rates of 1000 L/h and 500 L/h at the same pressure of either 5 bar or 20 bar, it can be stated that a higher feed flow results in a higher flux due to the smaller boundary layer and therewith lesser concentration polarisation. Having a look at the differenceadue to the different feed concentrations in **Figure 2 (b)** the flux is much lower at the higher feed concentration as could be expected.

Figure 3 shows the pure water flux over different pressures from 5 to 15 bar for the same membrane during different times of the experiments. Comparing the line at the beginning with the lines during the experi-

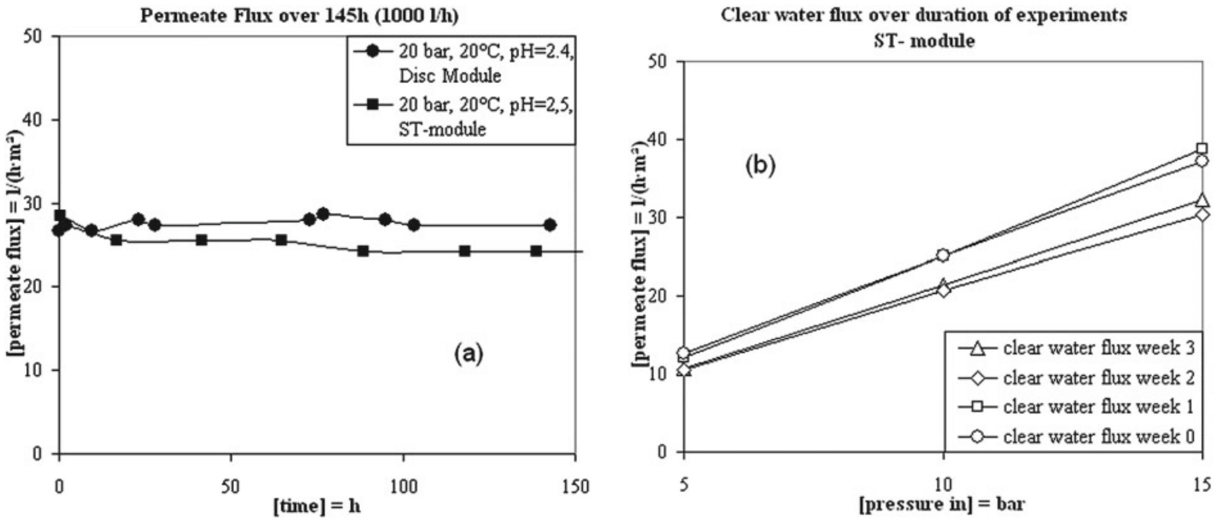

***Figure 4**. (a) Permeate flux over time for ST® module compared with flux over time for disc module. (b) Clear water flux at different times of experiment from the beginning (0 weeks) to the end after 3 weeks.*

ment the flux and inclination of the line are slightly lowered, but no significant flux decline has occurred as would be expected in membrane processes [3, 7d. This is supported by the graphs in **Figure 2** where there is also no significant flux decline over the 145 h duration of each experiment. The clear water flux and the flux of the permeate of the model water is in the same range as in previous experiments with small test cells [6].

Although there was no visible decline of the flux in the data collected, there was always some scaling observed in the backwaters of the permeate drain on the single discs of the disc module. This scaling consisted of a loose accumulation of crystals which could be easily rinsed off. In the experiments with concentrated model water a complete cover of this bulk scaling occurred between two plates in the middle of the module (near disc 80). Solid matter analyses of the scalant showed that the scaling consisted of gypsum. As can be seen in **Figure 2 (b)** with the flux recorded over time for the experiments with concentrated feed water, there is no visible drop in permeate flux. Lee and Lee [4] also report cases in which, depending on the operation conditions in nanofiltration of gypsum supersaturated solution, a saturation degree of 2.4 does not result in a significant drop in flux.

3.2 Spacer Tube® module

In **Figure 4 (a)** the flux over time of experiment is diagrammed over the duration of experiment of 145 h again. This time the permeate flux from the disc module MD 12 is compared with the flux from the Spacer Tube® module at the same feed flow rate of 1000 L/h and the same, normal concentration of the feed. It can be observed that the line of the ST® module rather follows a flux decline often observed for a membrane separation [4], than the line for the MD 12, where the expected decline could not be observed. The level of flux is comparable at similar conditions where the flux of the MD 12 is slightly above the flux of the ST® module.

An explanation could be the more turbulent flow through the disc module which reduces the concentration polarisation near the membrane surface but also results in a higher pressure drop of 5 bar in the MD 12 module, compared to 1 bar in the ST® module. This might also explain the slightly higher flux in **Figure 4 (a)** of the MD 12 compared with the ST® module at similar conditioa). The retention of single ions was nearly the same for both modules with a retention of >75 % to >95 % from 5 bar to 20 bar for each cation species for the concentrated feed and of >95 % for the normal model water. The sulphate retention was slightly lower but still >75 % and >95 %, respectively. The ion retention did not change distinctively over the time of the experiments. The rejection of total ions calculated for the whole time of experiment from total conductivity changed by a m. imum standard deviation of ± 0.01 %.

In the second part (b) of **Figure 4** the clear water flux of the ST® module is plotted in relation to pressures from 5 to 15 bar. The inclination of the lines represents data from different times during the duration of the experiments with the ST® module. Here the lines are declining more in a shorter time (in weeks) than in **Figure 3** (in month) for the MD12. This might also be supported by the graph showing a more obvious drop in flux for the ST® module. In general, the level of clear water flux of the ST® module in **Figure 4** is comparable with the level of clear water flux for the MD 12 in **Figure 3**, as well as with previous experiments [6]. A disassembling any inspection of the module was not done.

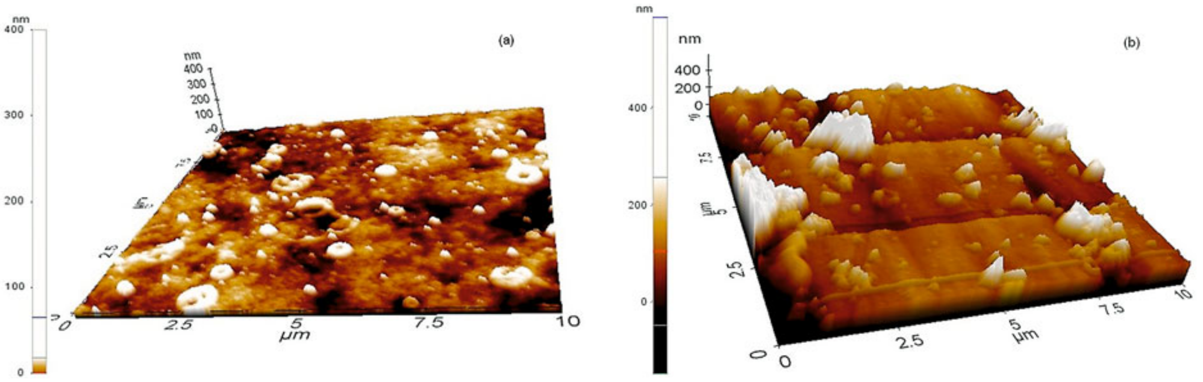

Figure 5. 3D AFM images of (a) unused membrane from the beginning of the experiments with MD 12 and (b) membrane from experiment no. 6 after two month of experiment.

Table 3. Root-mean-squared roughness for membrane samples from disc module before and after 2 month of experiment.

Sample	**root-mean-squared roughness (nm)**		
at time	1 x 1 µm^2	10 x 10 µm^2	50 x 50 µm^2
0 months	4.4	9.2	6.9
2 months	32	60.6	–

3.3 Atomic force microscopy

The membrane was characterizeh by atomic force microscopy in a non-contact mode to detect any changes in the membrane surface and composition. **Figure 5** shows the 3D AFM images of samples of the membranes from the disc module MD 12. Image (a) is the scan of a sample which was only used in the clear water experiment before the model water permeation experiment. Image (b) shows a scan of a membrane sample which was used in the MD 12 during two months of experiment. The scans are both in a dimension of 10x10 µm and scaled to a height of 400 nm for comparison. Thus, the colours marking the height cannot be compared directly, but have to be compared in relation to the legend bar along the left hand side of each figure. An overview of the root-mean-squared roughness [10] can be found in **Table 3**.g A direct comparison of the roughness with other results given in the literature should be done very cautiously because the data presented is the scan of one area on a sample only. To get a comparable characterization of the surfacee samples should be taken from differens areas of the membranasand the roughness should be calculated from different scan sizes of the same spos because the root-mean-squared roughness is scale dependent [10].

Even if there was no clear difference in clear water flux, comparing the two membranes scans shows that there is a difference between the new membrane and the membrane which was used over a certain time. It is not clear though what is the reason for the different appearance of the membrane scan. The elevations on scan (b) might be due to surface scaling on the membrans because bulk scaling was already detected. Also the abrasion of bulk scaling crystals or a change in the surface structure due to a low pH might contribute to the change in the surface when comparing **Figure 5 (a)** and **(b)**.

4. Conclusions

It was shown that highly saline mine water with a very low pH and a high content of sulphate and different metals can be successfully treated by Ny in a recycle experiment. The typical flux decline of a membrane process, still not distinctily, was observed in a ST® module while the disc module MD 12 did not show this significance. While a drop of the permeate flux due to membrane compaction or scaling was not observed directly, bulk scaling was found in the modules. Moreover, the AFM pictures show a difference in the membrane surface which indicates a modification of the membrane possibly due to surface scaling or a change in the membrane structure due to the low pH or abrasion. While the constant flux seems to be positive for the operation of NF in the treatment of acidic saline waters there obviously are limitations due to scaling and change of the membrane over time. As there is little scaling which does not lower the flux over 145 h, scaling might be more severe under practical conditions, where the composition of the water is more variable. Nonetheless, NF seems to be a capable alternative compared to reverse osmosis. There are no obvious disadvantages for removal of multivalent ions but the advantage of a higher flux to pressure ratio.

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