

## NEW MATERIALS FOR HIGH PRESSURE REVERSE OSMOSIS MEMBRANES

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High pressure reverse osmosis offers a huge potential for alternative applications in the field of evaporation. In systems with high osmotic pressures it is often necessary to operate with more than 10 MPa. In this pressure range the problem of mechanical deformation of the amorphous membrane material occurs, therefore membranes with better physical strength and durability are desirable. To reach that aim membranes were manufactured at our institute by plasma engaged chemical vapour deposition on a PTFE porous support. The produced samples showed promising properties concerning salt rejection in high concentrated sodium chloride solutions and especially concerning permeate flux under operating pressures up to 22.5 MPa.

### 1. INTRODUCTION

To run a reverse osmosis process, applied operating pressure has to compensate excessively the osmotic pressure of the system which is a consequence of the different concentrations on both sides of the membrane. High pressure reverse osmosis shall be defined by an operating pressure of 10 MPa or higher.

If reverse osmosis is used as an alternative process in the field of evaporation, high concentrations are often required e.g., in waste water treatment. The process must achieve very high water recovery rates (almost 100%), since all disposal methods for the concentrate are very cost intensive. Another example is the concentration of fruit juices with reverse osmosis, which is a very careful and aroma preserving treatment, compared with evaporation. Because of the usually high content of sugar and acids in the native juice a high pressure process is necessary to remove water from the juice.

But even in seawater desalination, the most important field of application for reverse osmosis membranes, a trend is observable to higher operating pressures. Pure water recovery should increase from 40% to 60% (Kurihara et al. 1999). This means that the osmotic pressure of the retentate will increase from 4.5 to 7.0 MPa. Operating the system at higher pressure releases more fresh water out of a pressure vessel, and this results in less energy and installation cost.

Apart from seawater desalination plants (where the recovery with even 60% compared with other applications is not very high), high pressure reverse osmosis units operate in combination with other reverse osmosis units at a lower pressure level. In a cascaded operation permeate of very high quality can be produced. Fig. 1 shows the flow diagram of a possible waste water treatment. The retentate of the 60 bar stage is further concentrated in a 200 bar stage, permeates of both stages are treated in a third stage to reach high quality.

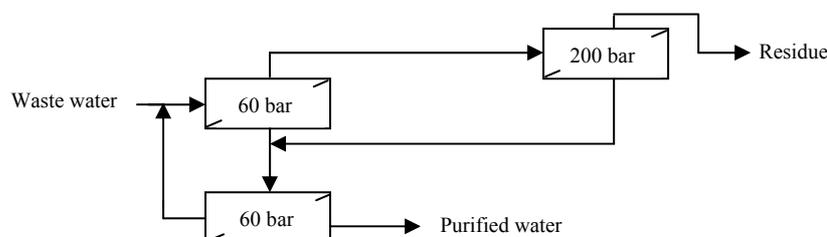


Fig. 1: Reverse osmosis cascade to produce high permeate quality

Although high pressure reverse osmosis up to operating pressures of 20 MPa can be considered as state of the art, membrane compaction is still a major problem for the process and a topic of interest for membrane and polymer scientists (Matsuura 2001).

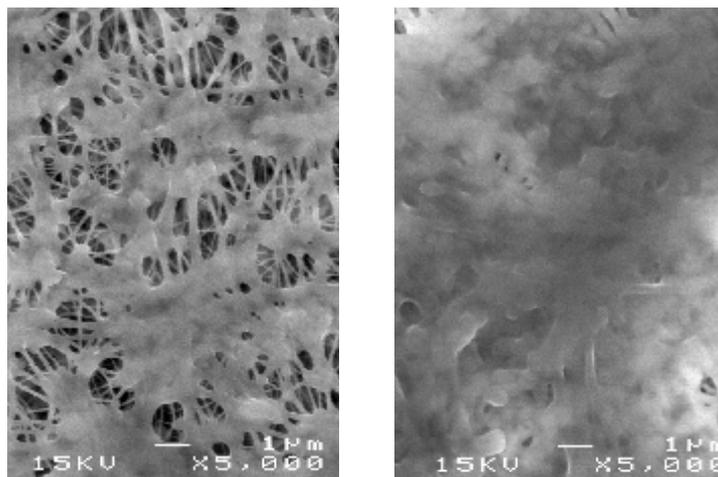
## 2. EXPERIMENTAL

In previous works at our institute dealing with commercial reverse osmosis membranes made of a porous polysulfone sublayer and a polyamide skinlayer we found that membrane compaction under high pressure operation, takes place at the porous sublayer rather than at the skin layer. Performance can be improved by giving the sublayer a more open structure (Kawada, 1999), this can also be done by plasma etching (Raab and Samhaber, 2001). In the presented work we looked for a totally new material to build the sublayer. Several materials have been tested e.g., melamin and PTFE membranes. PTFE membranes, as they are used in microfiltration, showed good results because of their open porous structure, additionally the material shows resistance against almost every chemical condition.

Experiments were carried out with flat sheet membrane samples of about 100 mm diameter. Because of the inhomogeneity of the tailored as well as the commercial membranes a lot of tests had to be done to get representative results. As commercial membrane a reverse osmosis membrane (Type AE) from Osmonics Desal was used.

### 2.1 Membrane formation in the plasma chamber

The plant consists of a cylindrical stainless steel vacuum chamber with two water cooled copper electrodes at a distance of 50 mm. Plasma was generated by a capacitive coupled 1,5 kW RF generator (13,56 MHz, Dressler MPG 1310). Power reflections were minimized by adjustment of a matching network. A PTFE support layer of about 100 mm diameter was fixed directly to the anode. The temperature of the anode was kept below 50°C. There were precursor materials used for the formation of the layer on the porous support like carbon in the form of acetylene, nitrogen in the form of ammonia and oxygen-gas. Nitrogen-gas was used as inertgas. The gas flow rate of the used precursors and the inertgas was set at 100 ml/min. The operation pressure in the vacuum chamber (10 Pa) was controlled by the adjustment of a valve. Plasma power was adjusted up to 600 W. There were periods of treatment between 2 to 20 min. After membrane formation process had been finished, vacuum was broken with air, and membrane samples were stored on air at least 24 hours before further use.



*Fig. 2: Porous support form PTFE untreated and after coating in the plasma chamber*

### 2.2 High pressure runs

The high pressure runs were conducted in a test cell where operating pressure is adjustable up to 30 MPa. The experiments were carried out with pure water and sodium chloride solutions, concentrated

up to 4 mol/l. To eliminate the concentration polarisation effect on the separation process, the salt solution in the cell was stirred. In the cell the membrane is placed on a stainless steel permeate spacer which drains the permeate flux. The active membrane area was 50 cm<sup>2</sup>. Before applying high pressure, the dry membrane flat sheets were flushed with demineralized water for two hours. To reach steady-state conditions, results were reported after a waiting time of 5 minutes.

Experiments started at a pressure of 2.5 MPa. Pressure was increased in 2.5 MPa steps up to 22.5 MPa. To show how high pressure influences unused membranes, special interest rested upon the first high pressure operation of every single membrane flat sheet. Differences in the performance of the membrane, which could be observed when pressure levels were reached several times, gave an impression of the irreversible compactations which took place at high pressure level.

The second point of interest was the performance level which the membrane reached after first high pressure use, therefore pressure increase up to 22.5 MPa and decrease down to 2.5 MPa was repeated several times with every tested sample.

### 3. RESULTS

According to the theoretical background of the well known solution-diffusion model (Eq. 1) the dependence of the permeate flow rate  $j_w$  on the operating pressure minus the osmotic pressure of the system ( $\Delta p - \Delta \pi$ ) which is the driving force for the process, should give a linear relationship. The slope of a plot  $j_w$  vs. ( $\Delta p - \Delta \pi$ ) should correspond to the membrane parameter A.

$$j_w = A (\Delta p - \Delta \pi) \quad [\text{m/s}] \quad (1)$$

In fact we observed this at the commercial membrane in the low operating pressure range ( $\Delta p$  below 7.5 MPa), but at higher pressure levels the deviation from equation 1 becomes stronger and at operating pressures above 17.5 MPa an increase of pressure results in almost no increase of permeate flux.

Raising filtration resistance caused by membrane compaction prevents further increase of permeate flux. Fig. 3 shows the pure water permeate flux (so  $\Delta \pi$  can be neglected) of the commercial membrane and the tailored membrane at their first use. It can be observed that the tailored membranes, contrary to the commercial ones, react with increasing permeate flux on every increase of pressure, even in the highest pressure range.

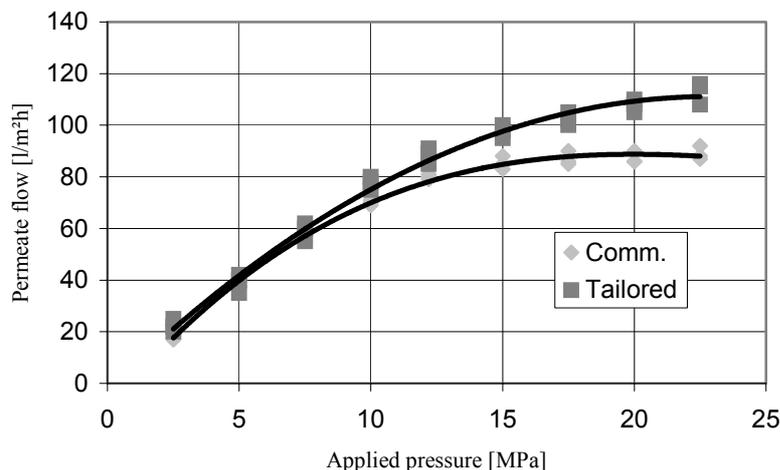


Fig. 3: Dependence of the permeate flow rate on the applied pressure, first use

After first use both types of membranes worked according to equation 1. A plot ( $\Delta p - \Delta \pi$ ) vs.  $j_w$  gave a linear relationship, but permeate fluxes were at lower levels than in the first run, which is a result of irreversible membrane compaction. Further decrease of permeate fluxes could not be observed in our experiments which took only little time, compared to the usual live time of a reverse osmosis membrane. Fig. 4 shows the results of the experiments with the used membrane samples. Now instead of pure water sodium chloride solutions were used for the experiments. Permeate quality was determined by conductivity measurements. Salt rejection of the tailored membranes (according to

Eq. 2) was above 90%, even at high concentrations. Salt rejection of the commercial membranes was above 96%.

$$R = 1 - \frac{\text{Concentration}_{\text{Permeate}}}{\text{Concentration}_{\text{Retentate}}} \quad (2)$$

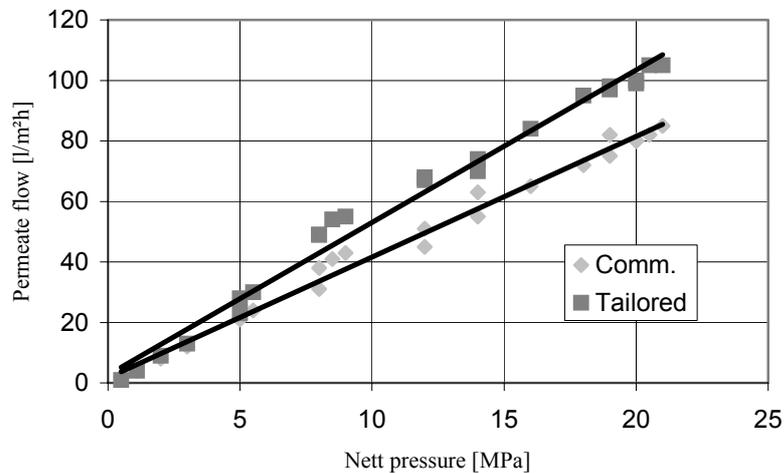


Fig. 4: Dependence of the permeate flow rate on the driving force after first use

Based on the concentrations of permeate and retentate the osmotic pressure of the system can be calculated. Operating pressure minus the osmotic pressure gives the net pressure which is the driving force for the process. Because of this calculation it is possible to compare the performance concerning permeate flux of both types of membranes, despite the different salt rejections.

According to the results of the experiments with pure water, the tailored membrane samples show better performance concerning permeate flux in the sodium chloride solution than the commercial one.

#### 4. CONCLUSION

Membranes were produced by plasma engaged chemical vapour deposition on a PTFE porous support. The produced samples showed sodium chloride rejections above 90% in almost saturated salt solutions. Under operating pressures above 20 MPa the plasma polymerised membranes exhibited higher permeate fluxes than commercial reverse osmosis membranes.

PTFE as support combined with the plasma polymerised skin layer results in a membrane with new properties concerning solvent resistance. The use of such a membrane could open a completely new range of applications for membranes in solvent recovery.

#### REFERENCES

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