

# Euromembrane 2000 highlights membrane physical characterisation and preparation techniques

Here we present the final instalment of our Euromembrane 2000 round-up. This is the third in a series of summaries covering the event, which was held in Israel during September last year. It considers the physical characterisation of membranes, and preparation techniques which are used to produce them.

Again based entirely on abstracts of papers which were presented at the conference, this thematic grouping highlights, among other things, the methods used for the direct measurement of the concentration polarisation phenomenon; electrochemical characterisation of membrane active layers, by measuring the transient membrane potential; silica scaling phenomena of reverse osmosis membranes; and a novel polymer foaming technique for the formation of membrane structures.

## Concentration polarisation phenomenon

A well known phenomenon occurring in membrane separation is the concentration polarisation near the membrane's surface. In nanofiltration and reverse osmosis this effect will give a retention that is different from the one calculated from bulk and permeate concentrations.

A quantification of the concentrations near the membrane is of great importance to understand separation mechanisms. The theoretical treatment of the concentration polarisation is given in the literature,<sup>[1]</sup> and is based on mass balances over the concentration boundary layer near the membrane's surface. The result is given by:

$$(c_m - c_p)/(c_b - c_p) = \exp(J/k) \quad (1)$$

where  $J$  is the flux through the membrane,  $k$  is the mass-transfer number (equal to the ratio of the diffusion coefficient and the concentration boundary layer thickness  $D/\delta_c$ ),  $c_b$  is the bulk concentration,  $c_m$  is the concentration at the membrane's surface, and  $c_p$  is the permeate concentration. Introducing the intrinsic retention  $R_{int} = 1 - c_p/c_m$ , Equation 1 can be rearranged into the well-known concentration polarisation modulus expression:

$$c_m/c_b = \exp(J/k) / [R_{int} + (1 - R_{int}) \cdot \exp(J/k)] \quad (2)$$

In order to calculate the concentration polarisation modulus, both direct methods, where the concentration polarisation is measured, for example using optical methods,<sup>[2]</sup> and indirect methods, which involve measuring the flux experimentally, while the mass transfer number is modelled with Reynolds, Schmidt and Sherwood numbers,<sup>[1]</sup> have been successful.

Edvard Sivertsen, Vetle Misje and Norvald Nesse, based in the Department of Chemical Engineering at the Norwegian University of Science & Technology in Trondheim, Norway have developed a direct method to study the concentration polarisation phenomenon near the membrane's surface. To the authors' knowledge, this is the first attempt to physically draw a sample of the solution near the membrane surface and analyse it. Their

conference presentation, 'Direct measurements of the concentration polarisation phenomenon', provided details of the approach.

## Capillary tubes

Through the top plate of a cross-flow, flat-sheet membrane cell, the authors mounted capillary tubes which could be exactly positioned vertically in the membrane cell-channel, above the membrane, using a micrometer screw with a scale of 0.01 mm. A micro-valve was connected to the capillary tube, allowing very small samples to be drawn for analysis. The height of the channel above the membrane was 3 mm.

## Representative samples

One major problem is to take representative samples from the tip position of the probe. If samples are drawn at a fluid velocity which is too high, it will create suction from the layers next to that under investigation. A sampling velocity of less than 10% of the flow velocity was found to be satisfactory.

Preliminary results indicate that the method will be useful in mapping concentration profiles through the boundary layers near a membrane's surface. In particular, it could be used for complex compositions of the feed cell. As an example, the concentration polarisation for a 0.1M MgCl<sub>2</sub> solution over an NF45 membrane (from Dow Denmark) was measured at 25°C, 20 bar and for different Reynolds numbers. The results are displayed in Figure 1. The results indicate a thinner concentration boundary layer at higher Reynolds number, and a steeper increase in concentration near the membrane for lower Reynolds number.

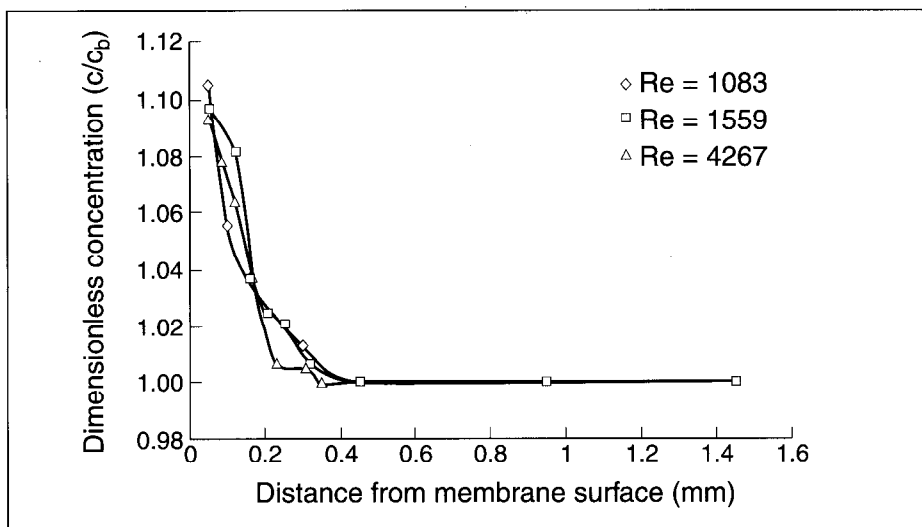


Figure 1. Concentration polarisation results for a 0.1M MgCl<sub>2</sub> solution at 25°C, 20 bar and for different Reynolds numbers. The membrane used was an NF45 membrane from Dow Denmark.

## Transient membrane potential

Electrochemical properties are important for the performance of reverse osmosis, nanofiltration and ultrafiltration membranes. They control the membrane fouling using charged foulants. In addition, the fixed electric charge is believed to be responsible for ion rejection — the so-called Donnan exclusion — by many nanofiltration membranes.

The determination of electrochemical properties of active layers of membranes for pressure-driven separation processes is complicated because of the multi-layer structure which is involved. This means that an applied concentration difference is distributed in usually an unknown proportion between the active layer and the support (in the measurement of steady-state membrane potential), or an internal 'concentrational' polarisation of unknown magnitude occurs at the boundary between the active layer and support (in Hittorf's technique). Therefore, only 'average' membrane electrochemical properties (including contributions from both the active layer and support) can be determined with steady-state linear electrochemical techniques.

To access the electrochemical properties of active layers, the research workers behind a paper entitled 'Electrochemical characterisation of membrane active layers through the measurements of transient membrane potential' (A. Yaroshchuk and Yu. Boiko of the F.D. Ovcharenko Institute of Bio-Colloid Chemistry, and A. Makovetskiy of the A.V. Dumanskiy Institute of Colloid & Water Chemistry, both part of the National Academy of Sciences of Ukraine) have developed a non-steady-state technique for the measurement of transient membrane potential — the so-called 'dab' technique.<sup>[3]</sup>

## Electrolyte solution

The membrane is equilibrated with an electrolyte solution, and is permitted to be in contact with it only on one side (the support side). The active side is suddenly touched with a 'pendant' drop of solution of a different concentration. The electrical circuit is closed, and the electrical response to this is tracked. Initially, the concentration gradient is located within the active layer, and the electrical response is governed by the ion transport numbers there.

The theory underlying the method reveals that the relaxation of transient membrane potential is characterised by a very broad dispersion, covering more than five orders of magnitude in time. This means that even when the characteristic relaxation time is as long as 1 s, the initial value can be directly observed only at times as short as 2 ms. Measurements taken at such short times may be essentially complicated by various circuitry interferences, and by the electrical response to the wetting of the active membrane's surface by the pendant drop. Therefore, the initial value of the transient membrane potential is often obtained through extrapolation to very short times. This procedure is relatively unambiguous, because the theoretical dependence contains only two parameters.

## Ceramic nanofiltration membrane

Measurements have been carried out mainly using a ceramic nanofiltration membrane of  $\gamma$ -alumina (supplied by the Inorganic Materials Research Laboratory, University of Twente, The Netherlands) in CaCl<sub>2</sub> and KCl solutions of various pH. The measurements have revealed that the active layer is positively charged within the entire pH range (4–7.3) and concentration (10<sup>-3</sup>–10<sup>-1</sup> mol/l) studied.

At the same time, a polymeric nanofiltration membrane (PES10) was negatively charged at pH 6. In many cases the experimental data could be fitted to theoretical curves, and the initial

values of transient membrane potential could be reliably determined. Some examples of experimental data with the corresponding theoretical fits are shown in Figure 2.

However, reproducible deviations from the theoretical pattern have also been observed. In these cases the extrapolation to very short times becomes less unambiguous. The possible causes for the deviations will be considered to improve the reliability of extrapolation.

The relaxation of transient membrane potential is essentially controlled by the salt (diffusional) permeability of the active layer. The same parameter is known to govern the initial slope of dependencies of salt rejection on the trans-membrane volumic flow in nanofiltration at sufficiently low pressures. To check the correlation, the authors have carried out sample measurements of salt filtration through the  $\gamma$ -alumina membrane.

## Good correlation

The correlation has been found to be very good, both in CaCl<sub>2</sub> and KCl solutions of several concentrations. Moreover, it has turned out that the measurements of relaxation of the transient membrane potential may be more suitable for the determination of diffusional permeability of active layers than the conventional filtration measurements.

The fact is that the initial slopes are often quite large, and their accurate determination calls for filtration measurement at very low pressures. The characteristic relaxation time is inversely proportional to the square of active layer diffusional permeability (*i.e.* it is quite sensitive to it). Its accurate determination is not a problem even where the initial slope is too large to be estimated from the filtration measurements.

In this way, the measurements of transient membrane potential are useful for determining the electrochemical perm-selectivity of active layers, as well as their diffusional permeability.

## Silica scaling phenomena

The conference also included a paper entitled 'Silica scaling phenomena of RO membranes', by

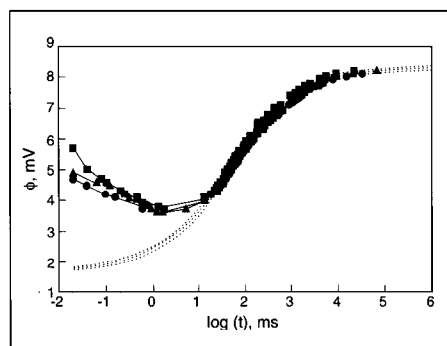


Figure 2. Transients of membrane potential, measured with the  $\gamma$ -alumina membrane by Ag/AgCl electrodes in 0.1M CaCl<sub>2</sub> solution: pH 7.3, ratio of concentration 2.

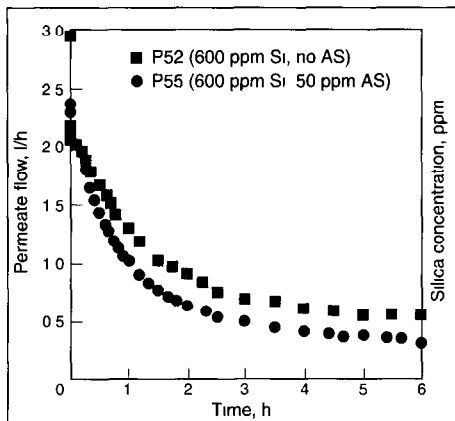


Figure 3. Permeate flow-rate decline.

Iris Sutzkover, David Hasson and Raphael Semiat of the Department of Chemical Engineering, WRI Rabin Desalination Laboratory at Technion — Israel Institute of Technology

This work forms part of an ongoing project which aims to determine permissible water recovery limits in desalting brackish water containing silica, and to assess objectively the relative effectiveness of different silica anti-scalants used to extend water recovery limits

### Difficult to predict

Threshold limits for silica scale deposition are difficult to predict because they are influenced by a large number of parameters, notably the pH and the specific salt composition. Moreover, silica deposition can take place in a variety of forms, differing in chemical composition and morphological structure through complex processes that may involve polymerisation steps, colloidal particle formation and coagulation phenomena

The reluctance to exploit silica-rich water stems from an inadequate understanding of the silica scaling system, the lack of a well established silica anti-scalant, and the difficult and costly efforts required to remove any silica deposit that may precipitate on a membrane

### Supersaturation conditions

Silica scaling occurs in a system exhibiting supersaturation conditions. The deleterious effects of scale deposition can be detected by the decline in permeate flux and by the drop in silica content of the solution. In their previous work, the authors developed a technique for fundamental analysis of scaling<sup>[4]</sup>

Scale deposition, occurring in RO desalting of saline feed solutions containing 100 ppm of silica, with and without anti-scalants, was examined. It was shown that the intensity of flux decline caused by silica scale deposition was well correlated with the intensity of the supersaturation level prevailing on the membrane

The specific objectives of the authors' present work were to explore the scaling mechanisms of highly supersaturated silica feed solutions where membrane scaling may involve processes

occurring both in the solution bulk and on the membrane surface

The feed solutions studied were at pH 7 and contained 2 g/l salts (CaCl<sub>2</sub> and MgCl<sub>2</sub>) and 600 ppm silica, with or without an anti-scalant, dosed at either 25 or 50 ppm. A run was carried out by circulating the feed solution through a tubular composite polyamide RO membrane (1 m long and with a diameter of 14.5 mm) for a period of 6 h at a flow velocity of 0.4 m/s, at a pressure of 40 bar. Both concentrate and permeate were recycled to the feed vessel.

Measurements were periodically taken of the permeate flow-rate and the solution turbidity. Both the dissolved and total silica contents of the recirculating solution were also periodically determined. At the end of each run, a membrane 'autopsy' was performed in order to elucidate the chemical composition and the morphology of the scale deposit by SEM photographs, EDS analyses and coating thickness measurements.

Analysis of the data extracted from numerous runs revealed several interesting phenomena. As illustrated in Figure 3, a severe flow decline was noted in all runs, most of which occurred during the first hour of operation. The extent of the decline during a run period of 6 h amounted to 80–90% of the initial flow. SEM photographs confirmed that roughly the same percentage of membrane area was obstructed by the scale deposit. No significant difference was noted in the runs performed with anti-scalant dosage.

EDS analyses disclosed that the scale consists of almost pure amorphous silica. Thickness and

weight measurements of the scale layer showed that the deposit formed in all runs was 40–50 μm thick, and was highly porous, with a bulk density of around 0.05 g/cm<sup>3</sup>.

### Surprising result

The most surprising result was revealed by the silica analyses (Figure 4). It was found that although the dissolved silica content declined dramatically during a run (from 600 ppm to about 200 ppm), the total silica content (as measured by ICP) remained substantially constant, after a slight decline of 5–10% during the first few moments of the run.

A material balance showed that the total mass of the silica deposit found on the membrane, which generated a permeate flow decline of 80–90%, was less than 1% of the total silica content in the feed, and less than 2% of the dissolved silica disappearing from solution.

Since silica depositing in the system was a very small fraction of the disappeared dissolved silica, the question arises of the whereabouts of the lost dissolved silica. Since no turbidity developed in the recycling solution, it appears that the dissolved silica remained in solution in the form of sub-micron-sized particles. A possible explanation is that the scale formation mechanism involves silica colloidal deposition on the membrane, followed by monomeric silica deposition, as suggested by Weres *et al.*<sup>[5]</sup>

(The authors wish to acknowledge with thanks the support of the Israel Science Foundation, the Middle East Desalination Research Center and

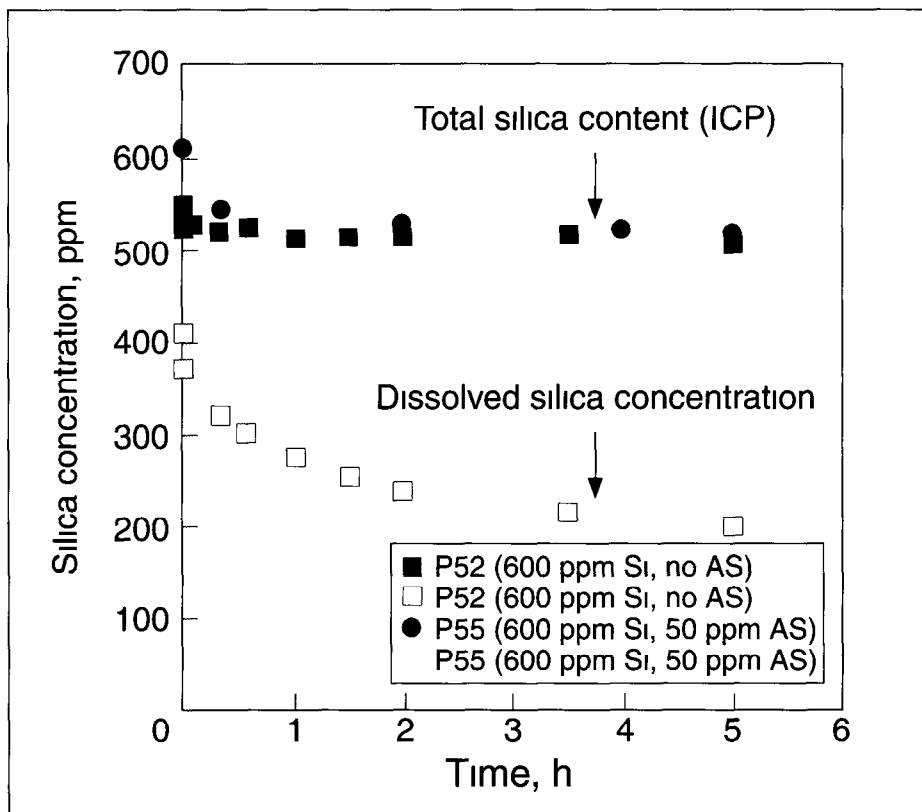


Figure 4. Dissolved and total silica concentrations.

Technion's Water Research Institute, with special thanks to Dr Roya Sheikholeslami of the University of New South Wales in Sydney, Australia for fruitful research collaboration)

## Parameters influencing the membrane-formation process

Polymeric membranes have found a wide variety of industrial applications over the years. Many of these applications require membranes with special properties, for example a specific morphology, pore size or pore-size distribution, solvent stability, or a special affinity for substances which are involved in the separation process. In short, membranes often have to be tailor-made.

The wet-phase inversion method is one of most widely used techniques for preparing asymmetric membranes. In this process the phase inversion takes place through the interaction of a liquid coagulation medium with a polymer solution, and takes into account the desired membrane format or shape (flat or hollow-fibre membranes).

### Mutual interdependence

During the phase separation, the polymer/solvent/non-solvent system is characterised by numerous interactions in the dope solution, as well as during the phase-inversion process (concentration of polymer solution, composition of polymer solution or coagulation medium, temperature and molecular weight). In this system it is important that the mutual interdependence of these parameters is realised, they are not isolated parameters.

These factors could be assigned to two important main areas of influence: thermodynamics and kinetics. The aim of this study, by T. Wegel, W. Albrecht, A. Christmann, R. Hilke and D. Paul of the Institute of Chemistry at the GKSS Research Centre GmbH in Geesthacht, Germany is to explain the correlation between influencing parameters of the membrane formation process and morphological features of the resulting membrane, using real membrane formation processes and model investigations.

The research work, which was detailed in a presentation entitled 'Kinetic investigations at the phase inversion process of polyetherimide membranes', focused on the determination of characteristic features of the phase-inversion process, which are able to describe the realistic membrane formation behaviour.

### Polymer foaming

Today, polymeric membranes are produced almost exclusively by phase inversion. Expensive, harmful and partly flammable solvents are often used in this process. These solvents have to be recycled because of cost and

environmental regulatory reasons, which require an expensive closed-cycle of the process streams.

### Open-cell or closed-cell structures

In addition to these disadvantages, the production rate may be limited by the rate of extrusion because of the slow liquid-liquid phase inversion process. These limitations may be avoided by using (supercritical) gases that can expand polymers to form open-cell or closed-cell structures (micro-cellular foams). In, for example, a high-rate extrusion process.

In a paper entitled 'Novel polymer foaming technique for membrane structure formation', B. Krause, N. F. A. van der Vegt and M. Wessling of the Membrane Technology Group, University of Twente in Enschede, The Netherlands discussed the use of carbon dioxide to produce membranes with tailored pore structures.

### Preparing micro-cellular foams

Several techniques can be used to prepare micro-cellular foams using gases in their supercritical and non-supercritical state as physical blowing agents. These techniques all rely on the same principle:

- the polymer is saturated with a gaseous penetrant (blowing agent) at high pressure,
- the polymer/gas mixture is quenched into a super-saturated state, either by reducing pressure or increasing temperature, and
- nucleation and growth of gas cells dispersed throughout the polymer sample evolves until all thermodynamic forces, driving mass transport, vanish.

Depending on the dissolved carbon dioxide concentration, and the polymer properties, cell sizes in the range of 1–10 µm were obtainable for amorphous polymers.

The presented results showed how the addition of certain low molecular weight additives can form open-cell polymer structures. These novel structures have been analysed, and their 'percolating' properties have now been documented. The research has shown that membrane structures, prepared through the use of foaming processes, are able to compete favourably with membrane materials prepared by the phase-inversion processes.

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**Further details on the research and projects covered by this article are available from the appropriate authors.**

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## Euromembrane 2000

Euromembrane 2000 was held at Ma'ale Hachamisha Kibbutz Hotel, in the Hills of Jerusalem, Israel, on 24–27 September 2000.

The conference included plenary lectures, oral presentations and posters. Parallel sessions allowed the programme to cover different aspects of membrane science and technology. The conference covered areas such as liquid membranes and membrane distillation, membrane characterisation, reverse osmosis, nanofiltration, ultrafiltration, microfiltration, gas separation, electro-membrane processes and membrane reactors. The event also emphasised desalination in arid zones and medical applications.

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