Processing and characteristics of TNO's hollow-fibre ceramic membranes

H.W. Brinkman, J.P.G.M. van Eijk, R.J.M. Creusen & R.A. Terpstra
Netherlands Organization for Applied Scientific Research (TNO)
Eindhoven & Apeldoorn, The Netherlands

The use of membranes is common practice nowadays in separation processes in the (process) industry, where conventional separation techniques are hardly an economically attractive alternative. Most of the membranes used here are made from polymeric materials. However, when high requirements are set on mechanical, chemical or thermal stability and when a long life time is requested, ceramic membranes are available. These membranes can be applied at relatively high temperatures, high pressures and/or pressure differences, or in aggressive/corrosive environments, for example during high temperature gas separation or separation of aggressive solvents. A big advantage of ceramic membranes when compared with polymeric membranes is that they can be steam-sterilised or cleaned with aggressive solvents; this is of importance in the food industry, where sanitary conditions are crucial.

Although flat and tubular hollow-fibre membranes are commercially available, the need for a new generation of low-cost ceramic membranes and membrane substrates with a high membrane surface/volume ratio has been ventilated numerous times. The ceramic hollow-fibre membranes that have been developed by the Netherlands Organization for Applied Scientific Research (TNO) fulfil this need. These membranes are more compact, e.g. have a surface-over-volume ratio of more than 1000 m^2/m^3, are easy to scale-up and are up to ten times cheaper.

TNO's particular focus is currently upon ceramic hollow-fibre membranes for microfiltration purposes. A considerable part of this article is dedicated to that area. However, since TNO wants to keep its leading position at the cutting-edge of ceramic hollow-fibre membrane technology, considerable efforts are also being made towards the application of top layers for ultra/nanofiltration and gas separation, and towards the development of high temperature resistant modules (up to 1000°C). These important subjects are dealt with in this article.

MANUFACTURING PROCESS AND CHARACTERISTICS OF ALUMINA HOLLOW-FIBRE MF MEMBRANES

In the past few years, a lot of experience has been gained with alumina microfiltration hollow-fibre membranes. Other materials that have been under investigation are silicon nitride, silicon carbide, hydroxy apatite, zirconia and perovskites.

As described earlier in International Ceramics [1], TNO's patented process for manufacturing ceramic hollow-fibre microfiltration (MF) membranes consists of three stages. In the first stage, ceramic powder is mixed on an approx. 1:1 volume base with a polymeric binder system at elevated temperatures, and granulated subsequently. In the second stage, this ceramic-polymeric mixture is shaped into a hollow-fibre by extrusion. Although extrusion is in principle a technique to generate products of infinite length, a practical length of the continuously-produced ceramic hollow-fibres is 40 cm. In the third stage of the process, the polymeric binder system is removed by a heat treatment up to 600°C, after which the fibres are heated further to a desired sintering temperature where the ceramic particles are more closely bonded to each other to give the porous hollow-fibre sufficient mechanical strength. In the case of alumina hollow-fibres, the sintering temperature is between 1150 and 1350°C.

Outer diameter	> 0.5 mm
Wall thickness	> 50μ m
Surface roughness	2-3 μm
Average pore size	0.1-1 μm
Porosity	30-50 %
Bending strength	up to 168 MPa
Burst pressure	> 220 bar (inside-out)
H2 permeation	12.9x10-6 mol/s.Pa.m2
Clean water flux	> 650 l/m2.bar.h

Table 1: Typical features of TNO's Al2O3 hollow-fibre microfiltration membranes

Typical characteristics of TNO's alumina hollow-fibre microfiltration membranes are given in Table 1.

The pore size distribution, average pore diameter and porosity of these alumina MF membranes are determined by mercury intrusion porosimetry. The average pore size and the porosity of the alumina hollow-fibres are mainly controlled by the initial particle size of the alumina particles and the

Batch	Average pore diameter (μm)	Porosity (%)	Clean water flux (l/m^2.bar.h)
A110698-3-P1300A-2	0.14	29	58
A270696-3-P1300A	0.14	33	160
A150895-1A-P1300D	0.22	38	418
A01197-3-P1300A	0.75	39	654
A230699-3A-P1300A-1	0.54	43	2100

Table 2: Processing conditions vs. membrane performance data

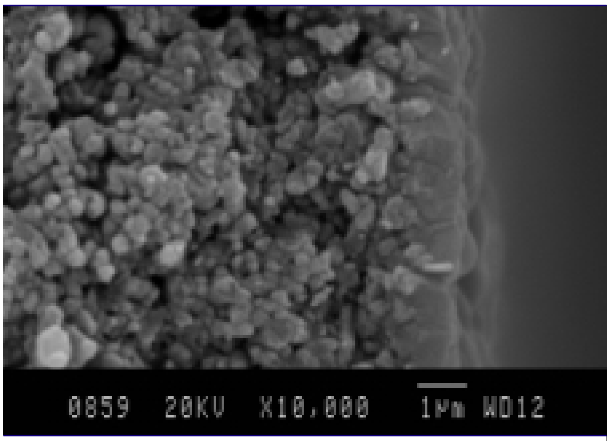

Figure 1: CVI-made silica top layer on an alumina hollow-fibre substrate

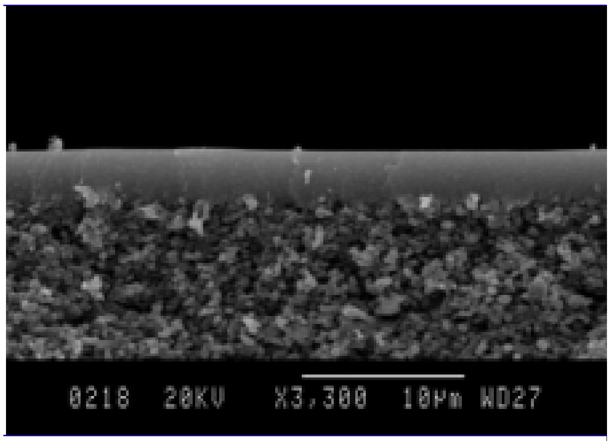

Figure 2: Wet chemically-applied g-alumina top layer on an alumina hollow-fibre substrate. The thickness of the top layer is approx. 3 mm, the average pore size 4 nm.

sintering temperature, respectively. Porosities of up to 50% have been obtained, with average pore diameters in the range of around 0.1 to 1 mm.

Clean water fluxes through TNO's alumina hollow-fibre MF;';;;;;;;..0:

Related to liquid permeation data, burst pressures have been measured which show that the hollow-fibres can withstand a pressure difference of 220 bars (inside out).

APPLICATION OF TOP LAYERS

Microfiltration membranes can operate as stand-alone membranes, e.g. for the separation of particles from liquid streams. However, as their surfaces are smooth and defect free, they can also serve as supports for highly selective top layers and, hence, form a new membrane system with new separation properties. At TNO several coating procedures have been developed, to be applied at the inside or outside of the hollow-fibre substrates. Application at the outside has the advantage that a larger membrane surface area will be formed. Application at the inside has the advantage that the top layer is not very vulnerable, but this is at the cost of a smaller membrane surface area.

However, when a top layer can be applied just inside the pore mouths at the outside of a hollow-fibre substrate, a desired combination of large 'top layer' surface area and low vulnerability is obtained. For this purpose, TNO applies the Chemical Vapour Infiltration (CVI) technique, where reactants in the vapour phase are transported to the porous substrate where they are transformed into a solid deposit. By taking the process conditions of the CVI process (temperature, pressure difference over the porous substrate, reactant concentration and flow velocity) as input parameters, the location of the deposit can be controlled. As two extremes, coatings can be applied on the inside and the outside of the hollow-fibres. A well-studied system also by TNO, in relation to the hollow-fibre substrates, is the formation of silica from TEOS (tetra ethyl ortho silicate, a metal organic precursor). By means of CVI it has been proven to be possible to modify the pores of macroporous (dp = 0.15 µm), uncoated alumina hollow-fibre substrates by depositing silica on the internal pore wall. When the process conditions are chosen well, the result of the CVI process is a microporous (dp < 1nm) silica membrane that is suitable for separating hydrogen selectively from a mixture of gases.

CVI is a relatively simple and, hence, relatively cheap membrane-manufacturing process. A microfiltration alumina hollow-fibre membrane that has been subjected to CVI is shown in Figure 1. Here we see a cross-section of the inside of the hollow-fibre, coated with a silica layer. In this case, the infiltration process was conducted for such a long time that not only the substrate pore exits have been modified and subsequently plugged with silica, but also a layer grew on top of the substrate. The layer thickness is approx. 1 mm.

Besides working upon vapour-phase based layer application techniques, TNO is also involved in the application of top layers by wet chemical procedures followed by a heat treatment. A recipe and a coating procedure have been developed for applying a g-alumina top layer (from a boehmite sol) on hollow-fibre alumina supports. As can be seen in Figure 2, homogeneous layers of high quality can be applied on hollow-fibre supports.

APPLICATIONS OF CERAMIC MEMBRANES

Typical applications of ceramic membranes are currently in beverage industries, for example beer or wine clarification, and concentration of fruit juices. An important aspect is that the membranes are neutral or inert as far as taste is concerned

Conventional separation techniques in wine making to stabilise the product consist of decantation, fining, cold treatment and filtration. Cross-flow microfiltration and ultrafiltration in general have been intensively evaluated in recent years as a modern one-step separation process to replace clarification, sterilisation and stabilisation of crude wines. More specifically, cross-flow ceramic microfiltration and ultrafiltration membranes have the potential to replace all the above-mentioned separation steps except cold treatment. When using ceramic membranes for removing bacteria, or yeast of suspended particles, the choice of the pore size is very important in determining the permeating flux and the rejection performance of these materials from wines. Since high fluxes are an important issue, TNO's membranes with a clean water flux of 654 l/m^2.bar.h (see Table 2) can be applied in wine filtration applications.

In the beer producing industries, the use of ceramic microfiltration membranes is a feasible alternative to the pasteurisation process with the potential advantage of avoiding heat exposure of the beer, and hence oxidation of some aroma compounds. By choosing the proper pore size of the membrane, those particles or organisms otherwise passing through the filtration process can be captured by the microfiltration membrane, thus improving the quality of the clarified beer.

An important potential application of ceramic membranes is their use in a catalytic ceramic membrane reactor. These membrane reactors will play a key role in the 'chemical factory of tomorrow', where process integration, energy reduction, continuous processing and compactness of equipment are important items. In a membrane reactor, catalysed chemical reactions, gas/liquid separations and heat exchange are combined in one compact device.

TNO'S ROLE IN CERAMIC MEMBRANE TECHNOLOGY

TNO's expertise on ceramic membrane technology is summarised thus:

- Consultancy on ceramic membrane technology
- Commercialisation of ceramic membrane technology
- Technology transfer from universities and research organisations to industry
- Manufacturing of ceramic hollow-fibre membranes
- Design
- Manufacturing of microfiltration membranes by extrusion
- Application of highly selective top layers by wet chemical and chemical vapour infiltration techniques
- Manufacturing of high-temperature ceramic membrane modules
- Materials characterisation
- Testing of membrane performance, application-oriented research

REFERENCES

[1] R.J.M. Creusen, R.A. Terpstra, J.P.G.M. van Eijk & A.E. Jansen, "Solving separation problems by using ceramic hollow-fibre membranes (MF)", International Ceramics Issue 2 (1997), 105-107

BIBLIOGRAPHY

Eddy Brinkman is project leader at TNO Ceramic Technology Department in the area of ceramic membrane technology and advanced ceramics processing. He received his PhD in 1994 at the University of Twente, The Netherlands, on the subject of manufacturing and modification of ceramic membranes. Before joining TNO in 1996, he was a researcher at the Netherlands Energy Research Foundation where he was involved in ceramic membrane technology.

Joost van Eijk is a project leader at TNO Ceramic Technology Department where he is involved with others in R&D in the field of advanced ceramics processing and ceramic membranes. He has been working at TNO since 1988.

Raymond Creusen has been involved for over 16 years in R&D in the field of membrane technology. Activities varied from membrane development to module and process development. At present he is working as senior project leader in the Chemical Engineering Department of the TNO Institute of Environmental Sciences, Energy Research and Process Innovation.

Rinse Terpstra is manager of TNO Ceramic Technology Department, where he is involved in R&D and consultancy in the field of processing advanced and traditional ceramics. He received his PhD in 1985 at the University of Nijmegen, The Netherlands, on calcium phosphates. Before joining TNO Ceramic Technology Department in 1990 he worked as a consultant for the traditional ceramics industry in 1985/86. From 1986 to 1990 he was project leader and head of department at the Netherlands Energy Research Foundation. ■

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