Review Paper

TESTING OF MICROFILTRATION CERAMIC MEMBRANES

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INTRODUCTION

Thanks to its low energy demands and favourable ecological characteristics, membrane filtration belongs among the dynamically developing technologies which have been finding wide application in many fields, in particular as fully adequate substitutes for classical technologies. The manufacture and subsequent selection of membranes is one of the basic problems in the implementation of membrane operations, where the following requirements have to be met:

- high specific throughput (permeability),
- high separating capability (selectivity),
- chemical, thermal and mechanical resistance to the effects of the substances treated and to the working environment,
- invariable technological characteristics during operation,
- resistance to mechanical damage during instalation, transport and storage,
- reasonable price.

The above factors are above all influenced by the choice of materials of which the membranes are made. In the manufacture of the membranes, polymeric materials (cellulose derivatives, acrylates, polyamides, polysulphones, polyesters, polyvinyl chloride, polypropylene, polycarbonate, fluoroplastics, etc.), as well as inorganic materials such as glass, carbon, sintered metals and special types of ceramics can be used. The selection depends primarily on the type of substance to be filtered, and on the conditions of the respective separating operation.

INORGANIC MEMBRANES

Inorganic membranes are nowadays utilized on an industrial scale in microfiltration and separation of gases. However, their application in ultrafiltration, reverse osmosis and pervaporation is also being studied [1].

Selection of the suitable type of membrane for a particular application depends on the concrete conditions of the process. However, it is possible to find certain properties common to all types of inorganic membranes predetermining them for a wider field of applications. The most important properties include chemical, thermal, mechanical and microbiological durability, and consequently a ready regeneration and sterilization. On the side od disadvantages, there are the difficulties involved in the manufacture of the membranes, due to the necessity of individual testing after each production stage, their considerable weight, and the higher price. There are several methods for the preparation of inorganic membranes, described e. g. in [2 through 12].

According to the material used in the manufacture, the commercially produced inorganic membranes can be divided into the following four groups:

- membranes of glass,
- membranes of carbon and of pure metals,
- membranes of inorganic polymers,
- ceramic membranes based on Al_2O_3, ZrO_2, TiO_2, or mixtures of these oxides.

The membranes differ in particular in their durability, pore sizes and the pore size distribution, the type of support, and their shapes (disks and plates, tubes, multichannel elements) [12]. At present, ceramic membranes based on alumina have found the widest range of industrial applications.

Ceramic membranes of aluminium oxide (alumina)

This type of membranes is most frequently prepared from α- and γ-modifications of Al_2O_3. Microfiltration membranes and porous supports of ultrafiltration layers are made of α-Al_2O_3 which resists relatively high pressures and temperatures, so that the membranes can be readily sterilized with steam or cleaned by backflushing. This material is also highly

Table I

Characteristic properties of ceramic membranes manufactured by TERRONIC a. s., Hradec Králové

	Porous support[1]	Two-layer membrane	Three-layer membrane
Composition	min. 95% Al_2O_3	min. 95% Al_2O_3 min. 99.5% Al_2O_3 (active layer)	min. 95% Al_2O_3 min. 99.5% Al_2O_3 (active layers)
Mean pore size [μm]	1.2 – 1.5	0.2	0.1
Water flux[2] [l/m^2h]	10,000 – 12,000	500 – 900	300 – 500

[1] Porosity 0.55–0.60

[2] Measured under the pressure of 100 kPa

resistant to acids, alkalies and various organic solvents.

The research of materials for ceramic microfiltration membranes at TERRONIC a. s. Hradec Králové is aimed at the utilization of corundum (α-Al_2O_3). Materials with a high permeability and strength (mean pore size 1.4 μm) are utilized as supports for multilayer membranes. The Company has gradually succeeded in developing a series of membranes of single-, double- and triplelayer types (a narrow pore size distribution), covering the entire microfiltration range (see Table I).

METHODS FOR TESTING MICROFILTRATION CERAMIC MEMBRANES

The testing of microfiltration and ultrafiltration membranes is aimed at determining the basic chemico-physical properties and at describing the geometry of the porous structure; also established are the flux characteristics of fluids (air, water) and the separating capabilities of the membranes.

Knowledge of the structure and properties of micro- and ultrafiltration membranes is of great significance for dealing with the theoretical problems of membrane processes, as well as for their successful industrial applications. The membrane manufacturers mostly specify data on the ranges of pH, temperature and pressure, and possibly on the permeability of the membranes and on the retention of certain molecules under defined conditions. However, in most instances they failure to give information on the structure and size of pores, which is highly important for the purpose of comparing various types of membranes with respect to their applicability for a certain separation process, for assessing the quality and selectivity of a membrane, and possibly for determining the effect of the conditions of preparation of the membrane on its final properties.

So far, there are no standard methods for testing, classification and evaluation of the properties of ceramic membranes. The present contribution is therefore aimed at describing some suitable methods for testing the basic characteristics of the porous structure of tubular membranes, and at correct interpretation of the test results. Special attention is paid to the permeability of membranes for gases and liquids, to the determination of the maximum pore size (bubble point and integrity test), and to the determination of pore size distribution.

Determination of permeability for fluids

Determination of permeability for gases and liquids is one of the important characteristics of the porous structure of membranes. The literature (e. g. [10, 12 through 14]) mostly specifies data on permeability for water or for air, under a given pressure and at a given temperature. From the standpoint of correct interpretation of results and the possibility of comparing various types of membranes, an important role is played by the exerimental arrangement, construction of the test cell (sample holder), preparation of the membrane for measurement, and last but not least, by the purity of fluids passing through the membrane. In some instances, in evaluating the results one has to take into account the character of the flow and the compressibility of the flowing gas, the change in the area of the membrane in the radial direction (in the case of single-layer tubular membranes) and clogging of the membrane with impurities possibly present in the test fluids [15].

Determination based on fluid flow through a wetted membrane

The method [16 through 25] has found a wide application particularly in determining the maximum pore dimensions, primarily because it is non-destructive and the membrane already tested can be employed for performing the separation tests.

A liquid with a low surface tension and a low volatility, which wets the membrane, is held in the pores by capillary forces (the forces of interphase tension) against the force of pressure difference Δp, which is trying to force the liquid out of the pores. On the assumption that the membrane is composed of a system of straight capillaries of circular sectional area with diameter d, passing throughout the entire membrane thickness, when the pressure difference attains the value (according to the Laplace equation)

$$\Delta p = \frac{4\sigma \cos \phi}{d} \qquad (1)$$

where σ is the surface tension of the fluid, and
ϕ is the wetting angle,

the liquid will be forced out of the pore and the fluid (air, nitrogen) will be forced through. The moment of opening up of the maximum diameter pores is indicated visually by the appearance of bubbles above the membrane surface. From the pressure difference measured and knowledge of the surface tension of the wetting liquid, equation (1) allows the maximum pore diameter to be calculated. According to the time course of pressure decrease inside the membrane saturated with a wetting liquid (the so-called integrity test) one can establish whether the membrane contains pores with sizes larger than that corresponding to the maximum value admissible for the given series of ceramic membranes.

Determination of pore size distribution

The method based on flow of a fluid through the membrane can likewise be used to determine the pore size distribution by evaluating the dependence of the rate of flow of gas through the membrane under a pressure difference, for both a wet and a dry sample having a maximum pores size over the range of 0.1 to 15 μm.

If the membrane contains pores of various diameters (which is the case of real membranes), an increase in pressure will lead to forcing the liquid out of the smaller-size pores and the permeability will increase to a certain value. The process is usually characterized by a non-linear dependence of the volume rate of gas flow on the pressure difference, $\dot V = f(\Delta p)$. For a dry, non-wetting membrane sample, this relationship is linear over the range of laminar flow (Fig. 1).

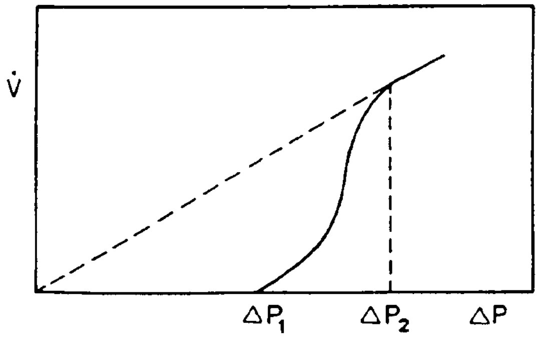

Fig. 1. The dependence of gas flow rate on pressure difference for a wetted membrane.

At a pressure difference lower than $\Delta p_1 = (2\sigma/r_{\mathrm{max}})\cos\phi$, the membrane is impermeable for the fluid. At a pressure difference of Δp_1, flow starts through the largest pores. With increasing pressure difference, increasingly smaller pores are opened up, while the rate of flow through one pore, $\dot v$, is given by Hagen-Poiseuille's equation

$$\dot v = \frac{\pi r^4 \Delta p}{8\mu L} \qquad (2)$$

where μ is dynamic viscosity, and
L is the pore length.

The total rate of gas flow, $\dot V$, through the membrane can be expressed by the equation

$$\dot V(\Delta p) = \int_r^{r_{\mathrm{max}}} \mathrm{d}\dot V = \frac{S\Delta p}{8\mu L}\int_r^{r_{\mathrm{max}}} r'^2 p(r')\mathrm{d}r' \qquad (3)$$

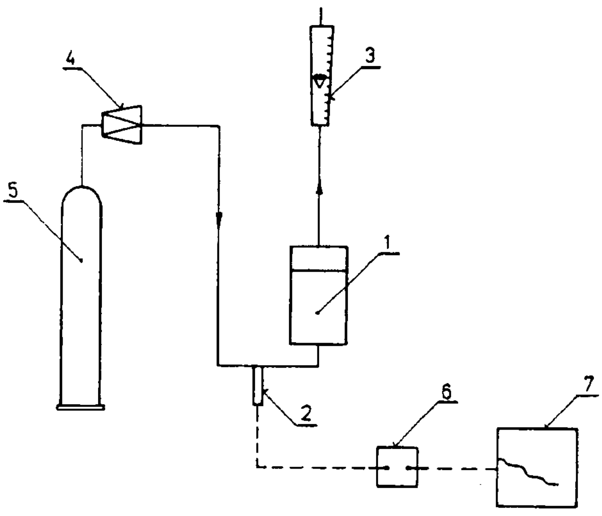

Fig. 2. Schematic diagram of the apparatus for the determination of pore size distribution. 1 – sample holder, 2 – pressure transducer, 3 – flow rate sensor, 4 – reduction valve, 5 – gas cylinder, 6 – stabilized current source, 7 – recorder

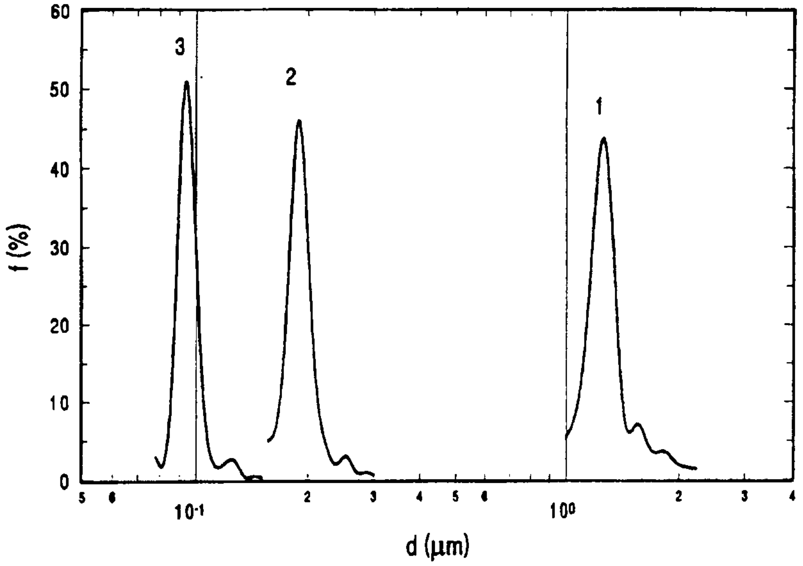

Fig. 3. Comparison of experimentally established pore size distribution in membranes made by TERRONIC a. s. 1 – porous support, 2 – double-layer membrane, 3 – triplelayer membrane

where S is the surface area of the sample, and
$p(r')$ is the active pore area distribution function.

At a pressure difference of $\Delta p_2 = (2\sigma/r_{\min})\cos\phi$, the smallest pores become permeable. The rate of flow then increases proportionally with further increasing pressure difference. The pore radii then lie over the range from $r_{\max}$ down to the minimum value $r_{\min} > 0$.

The pore size distribution in ceramic membranes can be determined on the apparatus shown schematically in Fig. 2. Gas from cylinder 5 passes via reduction valve 4 to the bottom section of measuring cell (sample holder) 1 and through the wetted membrane. The gas pressure is measured in the bottom section of the cell by pressure transducer 2. The rate of flow of gas passing through the membrane is measured by sensor 3. The pressure difference measured by the tensometric transducer is recorded by recorder 7, the current being supplied by stabilized current source 6.

Mathematical processing of the experimental data [17, 25] allows the pore distribution to be determined, and the maximum pore size $r_{\max}$, the minimum pore size $\mathrm{r}_{\min}$, the mean pore size $\bar{r}$, the standard deviation $\bar{s}_r$ and the relative width of distribution α to be calculated. To interpret correctly the experimental data obtained, it is also necessary to take into consideration the character of the flow and the compressibility of the flowing gas, the change in the active area of the membrane in the radial direction (with single-layer tubular membranes), and the possible effect of Knudsen's diffusion. An example of experimentally established pore size distributions for a porous support, and a double- and triple-layer membrane is shown in Fig. 3.

The pore size distributions of two different types of ceramic membranes are illustrated in Fig. 4. The picture shows that the two membranes with similar mean pore sizes exhibit quite different courses of pore size distribution, and also differ substantially in their permeability for pure water. This fact will be decisive for selecting the suitable type of membrane for the respective separation process.

GENERALIZATION OF THE METHODS

The behaviour of each type of membrane during a given separation process is significantly influenced by the character of the mixture being separated. From this point of view, all of the methods for the testing of membranes mentioned above are merely primary guides for the selection of certain membranes in a given type series, because other laboratory experiments with the system membrane-substance to be separated are indispensable for determining precisely the separation characteristics of the membranes and their throughputs.

The results of permeability tests may serve above all for classifying and characterizing the membranes produced within the framework of one manufacturing batch. The maximum pore size determinations and the integrity tests are important especially in the pre-application testing in fields where the separation selectivity must be painstakingly satisfied (e. g. in the food or pharmaceutical industries). The pore size distribution is a significant characteristic of membranes

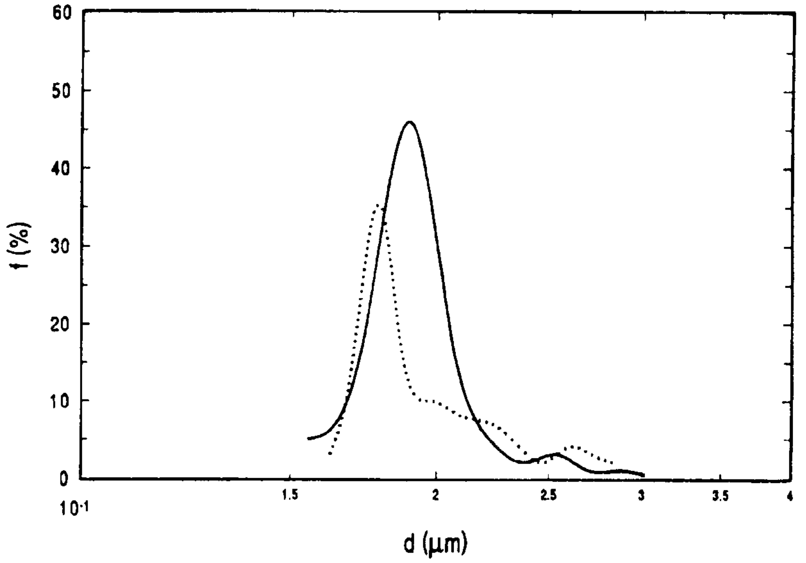

Fig. 4. Comparison of experimentally established pore size distribution in two types of ceramic membranes.
(——) single-layer membrane, mean pore size $d = 0.198$ µm, water flux $J_0 = 60$ l/m^2h
(......) double-layer membrane, mean pore size $d = 0.215$ µm, water flux $J_0 = 860$ l/m^2h

in the course of their manufacture. It is used to compare various types of membranes and is partially decisive for the selection of a membrane for a certain separation process.

CONCLUSION

The literature as well as practical experience show that the methods based on determining the rate of flow through the membrane are suitable for testing the microfiltration membranes in the course of their manufacture and directly before their application. In spite of the advantages of these tests, there is not yet a method which would cover all of the significant process parameters in a complex way. And this is why in implementing the membrane process, attention should be paid primarily to the mutual relations between the performance properties of the membrane (retention of particles, filtrate flow) and the properties associated with the material and structure of the membrane (pore size distribution, pore density, chemical and electrical characteristics of the membrane surface).

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