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WATER TRANSPORT PROPERTIES OF CERAMIC MICROFILTRATION MEMBRANES

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This paper deals with both theoretical and experimental study of the transport of water through α-alumina microfiltration membranes. A simple model combining the ideas of the capillary flow and the flow around solid bodies has been tested as a means for the prediction of the hydraulic resistance in the flow of water through the ceramic membrane structure.

Introduction

While membranes used for industrial separations have been and continue to be made primarily from organic polymers, a significant amount of attention over the past decade has been focused on porous ceramic membranes. The motivation for this interest stems from the notion that ceramics are more thermally and chemically stable that most of polymers. For example, ceramics can be used at significantly higher temperatures, have better structural stability without the problems of swelling or compaction, can usually withstand harsher chemical environments, are not subject to microbiological attack, and can be backflushed, steam sterilized or autoclaved[1].

The efficiency of a membrane depends on both its ability to separate particles in a selective way, and on the flux which can be achieved across this membrane. Although some membranes possess a symmetric structure, in most cases they are asymmetric consisting of several layers coated on a bulk porous support and with a gradual decrease in pore size. The main advantages of an asymmetric structure are high fluxes and the ability to have tailored membranes made of materials different from the support.

However, the development of membrane processes is hampered by an unsatisfactory quantification of water transport. The flow of water is classically viewed as a laminar flow through a homogeneous porous medium where the entire hydraulic resistance is located exclusively in the active layer of the membrane. However, the transport of water through multi-layered membranes has not yet been quantified due to the existence of a transition boundary layer between two porous media of different particle sizes.

The aim of this work is to determine the decrease in the porosity at the interface between the membrane layer and the support layer by means of a simple model combining the ideas of the capillary flow and the flow around solid bodies. This would allow the hydraulic resistance of the boundary layer to be quantified. In order to check the infiltration effect theory, the transport of water through different α- alumina microfiltration membranes has been compared.

Hydraulic Rresistance Definition

The permeate flux u through a porous medium is usually described by the Darcy equation

$$u = \frac{\Delta P}{R\mu} \tag{1}$$

with ΔP being the driving pressure, μ the dynamic viscosity, and R the membrane hydraulic resistance.

The experimental resistance value can be derived from the plot of u against $\Delta P/\mu$, which is a straight line whose slope corresponds to $(1/R_{exp})$. By assuming the validity of the Kozeny-Carman capillary model, the theoretical resistance values can be predicted for each porous media by the equation[2]

$$R_{th} = \frac{180(1-\varepsilon)^2 L}{\varepsilon^3 d_g^2} \tag{2}$$

with ε being the porosity, d_g the particle diameter, and L the porous media thickness.

The relationship between the mean pore diameter d_p and the particle diameter d_g (considering spherical particles) is easily derived

$$d_p = \frac{2}{3}\frac{\varepsilon}{1-\varepsilon}d_g \qquad (3)$$

By comparing Eqs (2) and (3), a theoretical resistance can be written in the following form

$$R_{th} = \frac{80L}{\varepsilon\, d_p^2} \qquad (4)$$

In a filtration element containing multiple layers, the hydraulic resistance is evaluated by summing all the layer resistances. If a transition zone between the active layer and its support exists, another resistance, which can be evaluated by the same equation, needs to be taken into account.

Experimental

Membranes

The ceramic membrane used for testing was an alumina-based, tubular, internal-pressure-type membrane (manufactured by Terronic in the Czech Republic). It had an inside diameter of 6 mm, outside diameter of 10 mm, and was produced either as a thick α-alumina layer (mono-layered) or a thin α-alumina layer on the top of the support (multi-layered, see Fig.1). For this type of asymmetric membrane, the slip-casting method was used. The void volume of the mono-layered membrane samples was determined by liquid flooding and by measuring the membrane thickness. The pore size distributions of the membranes were also determined using liquid displacement technique[3]. In our characterization studies, several types of membranes were used with a nominal pore diameter from 0.1 to 0.4 μm. The main characteristics of the membranes are summarized in Table I.

Fig. 1 Cross-section of a three-layered alumina membrane

Equipment

The flow of water through α-alumina microfiltration membranes (length 20 mm) at various pressures was investigated using the apparatus shown in Fig. 2. The permeate mass and the filtration pressure data were synchronized by use of a pressure transducer interfaced with a computer. Therefore, simultaneous measurements of the cumulative permeate mass and the pressure were obtained. These measurements covered a range of constant filtration pressures (ΔP) from 100 to 300 kPa.

Table I Main characteristics of the α-alumina membranes used

Membrane	d_p, μm	ε	$u \times 10^4$ *), ms^{-1}
1 three-layered	0.091	0.48	1.42
2 mono-layered	0.103	0.38	0.03
3 mono-layered	0.175	0.42	0.08
4 double-layered	0.219	0.48	3.11
5 double-layered	0.250	0.48	3.61
6 double-layered	0.388	0.51	6.44
Membralox[4] three-layered	0.200	0.40	5.11

*) at 100 kPa

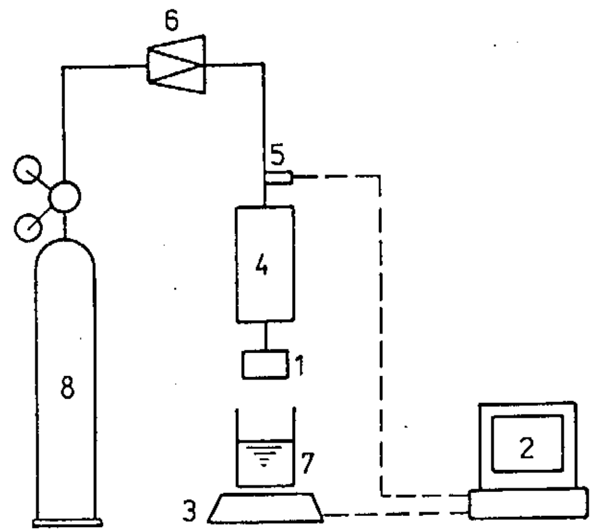

Fig. 2 Schematic drawing of the apparatus for determination of the water flux; 1 sample holder with membrane, 2 computer, 3 balance, 4 reservoir, 5 pressure transducer, 6 regulating valve, 7 permeate, 8 pressure source

Results and Discussion

When determining membrane rejection characteristics, an important parameter is the mean pore diameter of microfiltration membranes having a narrow pore-size distribution. In general, the smaller the pore diameter, the higher will be the rejection coefficient of particulates/solutes of a greater nominal size. However as the pore size decreases, the permeability to liquid also rapidly decreases. Typical pure water (prefiltered deionized water) fluxes as a function of the pressure difference are shown in Fig. 3 for different microfiltration alumina membranes. It is well shown in Fig. 3 that straight lines were obtained in conformity with Eq. (1).

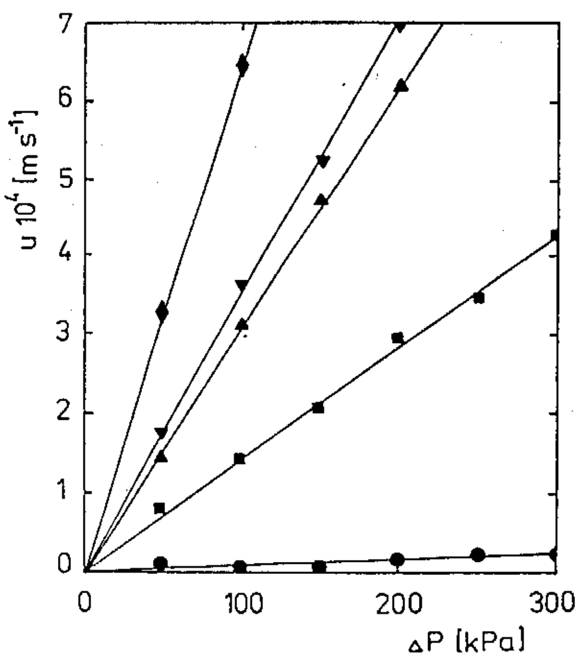

Fig. 3 Permeate flux of water u through various types of alumina membranes: ● - d_p = 0.175 μm, mono-layer; ■ - d_p = 0.091 μm, three-layered; ▲ - d_p = 0.219 μm, double layered; ▼ - d_p = 0.250 μm, double layered; ♦ - d_p = 0.388 μm, double layered

It is now possible to compare the experimental values R_{exp} and the calculated values R_{th} from Eq. (4) (Table II). The comparison highlights a discrepancy between the predicted and the measured values. More precisely, Eq. (4) gives a good prediction for all the mono-layered membranes, but does not allow the calculation of the resistance of the multi-layered membranes. This discrepancy cannot result from factors such as pore size distribution or tortuosity; otherwise the calculation would also be inaccurate for the mono-layered membranes. The observed differences could be due to an interfacial zone where two porous media of different particle size are interpenetrated.

The boundary layer effect is also quantified by the difference R_{bl} between $R_{\exp}$ and R_{th}

$$R_{bl} = R_{\exp} - R_{th} \qquad (5)$$

The Terronic 0.388, 0.250, and 0.219 μm membranes are composed of two media only, the active layer itself and its support, resulting in only one boundary layer. The Terronic 0.091 μm membrane and Membralox 0.2 μm membrane[4] have three porous media, i.e. the active layer, the underlayer, and the support. They have therefore two boundary layers.

A boundary layer between two media of different granular size is a transition zone particularly difficult to define geometrically. However, the thickness could be used to characterize the boundary layer as a first approximation. The thickness is evaluated from the very simple model illustrated in Fig. 4 which suggests a thickness of $D/2$, D being the mean diameter of the larger particles. An effective porosity value can then be derived from Eq. (2) and the data of Table II. By comparison with the porosity value in the bulk of a porous medium - being ca. 0.45 - it is obvious that a dramatic drop occurs in the porosity values in the transition zone to values between 0.18 and 0.25.

Table II Experimental and theoretical resistances of α-alumina membranes used

Membrane No.	$R_{\exp} \times 10^{-11}$ m^{-1}	$R_{th} \times 10^{-11}$ m^{-1}	$R_{bl} \times 10^{-11}$ m^{-1}	$R_{us} \times 10^{-11}$ m^{-1}	$R_{um} \times 10^{-11}$ m^{-1}
1	7.06	4.68	2.38	1.11	1.27
2	360	337			
3	120	117			
4	3.20	2.09	1.11		
5	2.77	1.70	1.07		
6	1.55	0.73	0.82		
Membralox[4]	1.96	0.75	1.21	0.32	0.89

Conclusion

Alumina microfiltration membranes with different properties were used to characterize their behaviour. A comparison was made of a flow through a mono-layered membrane with that through a similar multi-layered one. The simple model combining the ideas of the capillary flow and the flow around

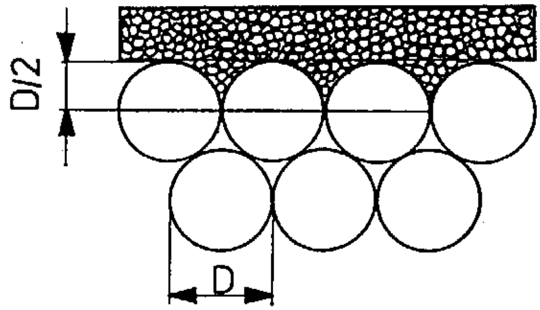

Fig. 4 Simple model of the interpenetration between two granular media of spherical particles

solid bodies at the membrane/support interface can predict the effect of the transition zone in the multi-layered alumina membranes which can induce both porosity and mean pore diameter decrease in the boundary layer. The accuracy of the results given by this simple model is limited by other parameters (like grain shape, size distribution, and sintering effect) which have not been taken into account in this model.

The information obtained from those results can be used to choose an optimum active layer/support combination for a particular application.

Acknowledgements

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Symbols

d_g	mean particle diameter, m
d_p	mean pore diameter, m
D	mean diameter of the larger particles, m
ΔP	pressure difference, Pa
R	hydraulic resistance, m^{-1}
R_{bl}	boundary layer resistance, m^{-1}
R_{exp}	experimental resistance, m^{-1}
R_{th}	theoretical resistance, m^{-1}
R_{um}	underlayer-membrane resistance, m^{-1}
R_{us}	underlayer-support resistance, m^{-1}
u	permeate flux, $m\,s^{-1}$
L	porous media thickness, m
ε	porosity
μ	dynamic viscosity, Pa s

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