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MATERIALS ASPECTS OF MICROPOROUS INORGANIC GAS SEPARATION MEMBRANE MANUFACTURING

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Abstract

Knudsen diffusion or ultrafiltration gamma alumina membranes with a pore size of 4 nm are not necessarily good enough as support for high selective (HS) microporous membranes due to irregularities and defects in the surface. By modelling it will be shown that there is a very detrimental influence of defects on the separation factor of these HS membranes. The development of a satisfactory support system will be reported.

Keywords

Ceramic membranes
Gas separation
Defects

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1. INTRODUCTION

Only when defect free high-selective and high-permeable microporous inorganic membranes can be manufactured with large surface areas, separation of gases with these membranes on an industrial scale is technically feasible. Production of tubular (or flat) substrates with large surface areas for the application of a high-selective membrane layer is quite different from that on substrates of a few cm^2. Micron size defects in the membrane layer, often originating from irregularities and defects in the substrate system, have a very detrimental effect on the separation performance. The larger the surface area of the membrane, the larger the chance that these defects will occur. For large scale application the processing of the substrate should be done in such a manner that intrinsically a smooth enough substrate surface for the application of a nearly defect free separation layer is obtained. Post-treatments such as polishing or multiple dipping of the substrate to achieve the demanded flatness is out of the question from an economic point of view but often also from a technical point of view.

From previous R&D concerning the development of multilayer membrane systems we have learned that pore defects above a certain size in a substrate have a tendency to be translated to the next layer. As expensive post-treatments need to be avoided we search for optimising towards a minimum defect density per layer and a minimum in coating operations. In this report we will show that an ordinary Knudsen diffusion gas separation membrane is not necessarily suitable as a substrate for the application of a high-selective separation layer on top of it. When a Knudsen diffusion membrane possesses defects with a certain pore size and pore density the membrane will still separate gases mainly by Knudsen diffusion. However, when the selective mechanism gives a higher selectivity compared to Knudsen diffusion, e.g. due to activated transport of one of the species, the overall permeability will generally be an order of magnitude lower and the influence of defects is very strongly increased. During manufacturing high-selective membranes generally defects in the support system such as large pores or irregularities will be translated to the separation layer. This causes this layer to be leaky to such an extent rendering the selectivity not higher than that of the Knudsen substrate. A solution for this problem is improvement of the support as we will argue and show.

2. THE "CLASSICAL" THREE LAYER KNUDSEN MEMBRANE

In the past we have developed a three layer Knudsen diffusion tubular membrane system: on the outside of a substrate tube an alpha alumina layer is applied by filmcoating. On top of this layer a gamma alumina layer, having a mean pore diameter of 4 nm, is applied (see figure 1a). We take this system as a starting-point.
The performance of this Knudsen diffusion membrane (van Veen 1991) is comparable to that reported by others. Maybe surprisingly the bubble point pressure (= pressure at which the first bubble is seen when a tube is emersed in a liquid and pressurised) of our classical Knudsen membrane tubes with a length of 80 cm was only about 0.5 bar in pure water. This means that the largest open pore from one side to the other side of the membrane is about 6 µm in diameter. The defect density of pores with a diameter of 4 µm is in the order of 1000 to 10000 per tube (length = 80 cm) or 0.1 -1/mm^2 (measured by bubble-frequency). The bubble point and defect density of the alpha alumina support system appeared to be about the same as for the complete asymmetric Knudsen membrane. This is an important argument in favour of the hypothesis of defect translation from one layer to the next layer.

Optimisation towards a defect free Knudsen system will improve the Knudsen diffusion selectivity only slightly as we will discuss further on. Our main motivation for improvement of the Knudsen system was the proposition that the classical Knudsen system is not suitable as a support for high-selective microporous membranes, because of the high defect density.

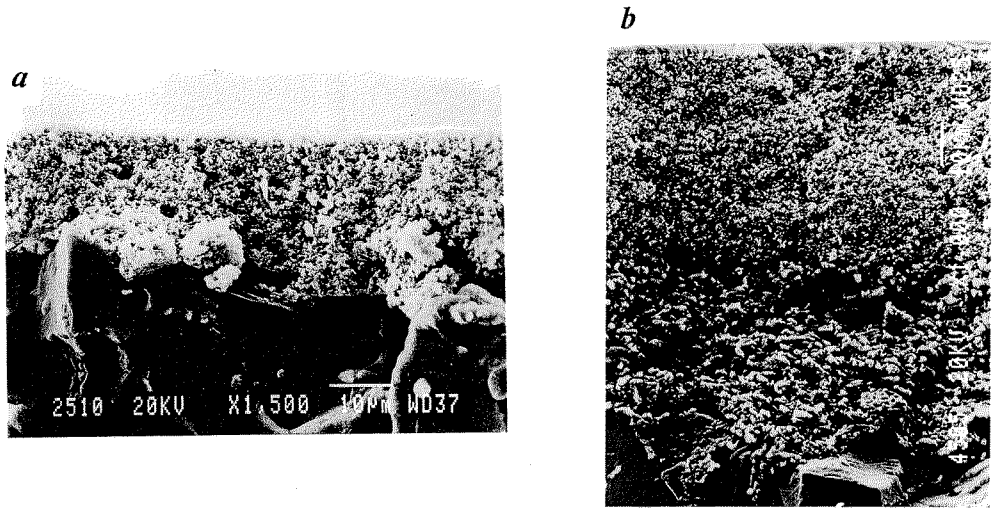
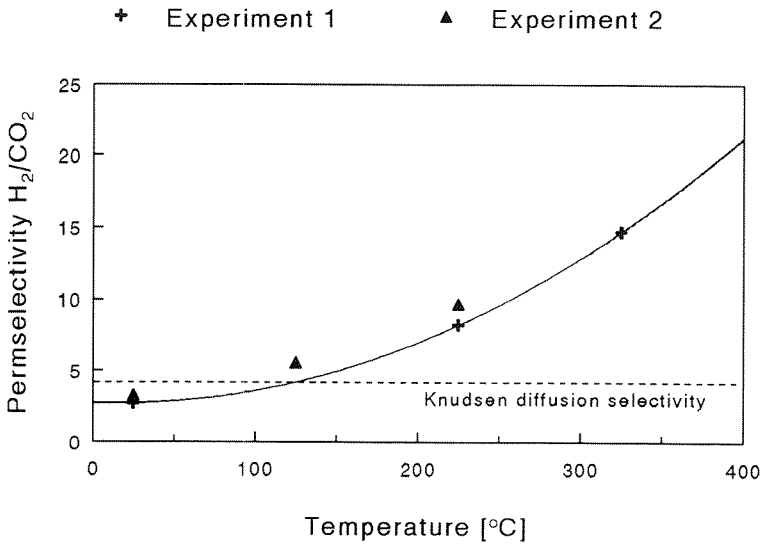


Figure 1 *Cross section of a) "Classical" Knudsen diffusion membrane and b) high-selective gas separation membrane support.*

3. MEMBRANE COATINGS BEYOND KNUDSEN DIFFUSION MEMBRANES

Like a number of other research groups we did some initial work on the sol-gel coating of our "classical" tubular membranes with a thin (100-200 nm) microporous silica coating. Because of our interest in high temperature H_2/CO_2 separation we have measured permeancies of these gases at temperatures up to 325°C. Some results are shown in figure 2. Although permselectivities higher than Knudsen have been obtained, it cannot be concluded from this that this membrane is a good gas separation membrane.



Figuur 2 *H_2/CO_2 permselectivity of high-selective silica membrane against temperature.*

The reason for this is that the permselectivity is calculated from the permeance of gases at zero pressure and is more a membrane material characteristic than a membrane process characteristic. The permselectivity determined at zero mean pressure contains absolutely no laminar flow contribution. In real applications the membrane operates at a mean pressure above zero with gas mixtures. Some non-selective laminar flow gas transport can then be very detrimental for the real selectivity, especially with membranes with very low permeability.

Further we found that the reproducible preparation of silica sols deserved more care then generally is reported in the literature. Reproducibility of the used procedures is of course an important factor for successfully concluding of our scaling up programme.

These findings motivated us to direct our research work towards improvement of the Knudsen support and silica sol synthesis and characterisation.

4. EFFECTS OF DEFECTS

Before starting an expensive optimisation development programme for the high-selective coating, we wanted to get an idea of how translated defects of the support would affect the performance of a microporous silica coating on a Knudsen support tube. We wanted to know what size and density of defects is still acceptable in the silica layer.
In order to get this information a simple numerical model of the multilayer membrane system was set up as shown as an electric analogue circuit schematically in figure 3. Gas fluxes and separation factors for gas mixtures could be calculated numerically on the basis of differential mass balances for the transport mechanisms in each layer, using the appropriate boundary conditions. Input parameters for the calculations are amongst others the layer thicknesses, porosity and pore size of each layer and an estimate of the tortuosity. Because

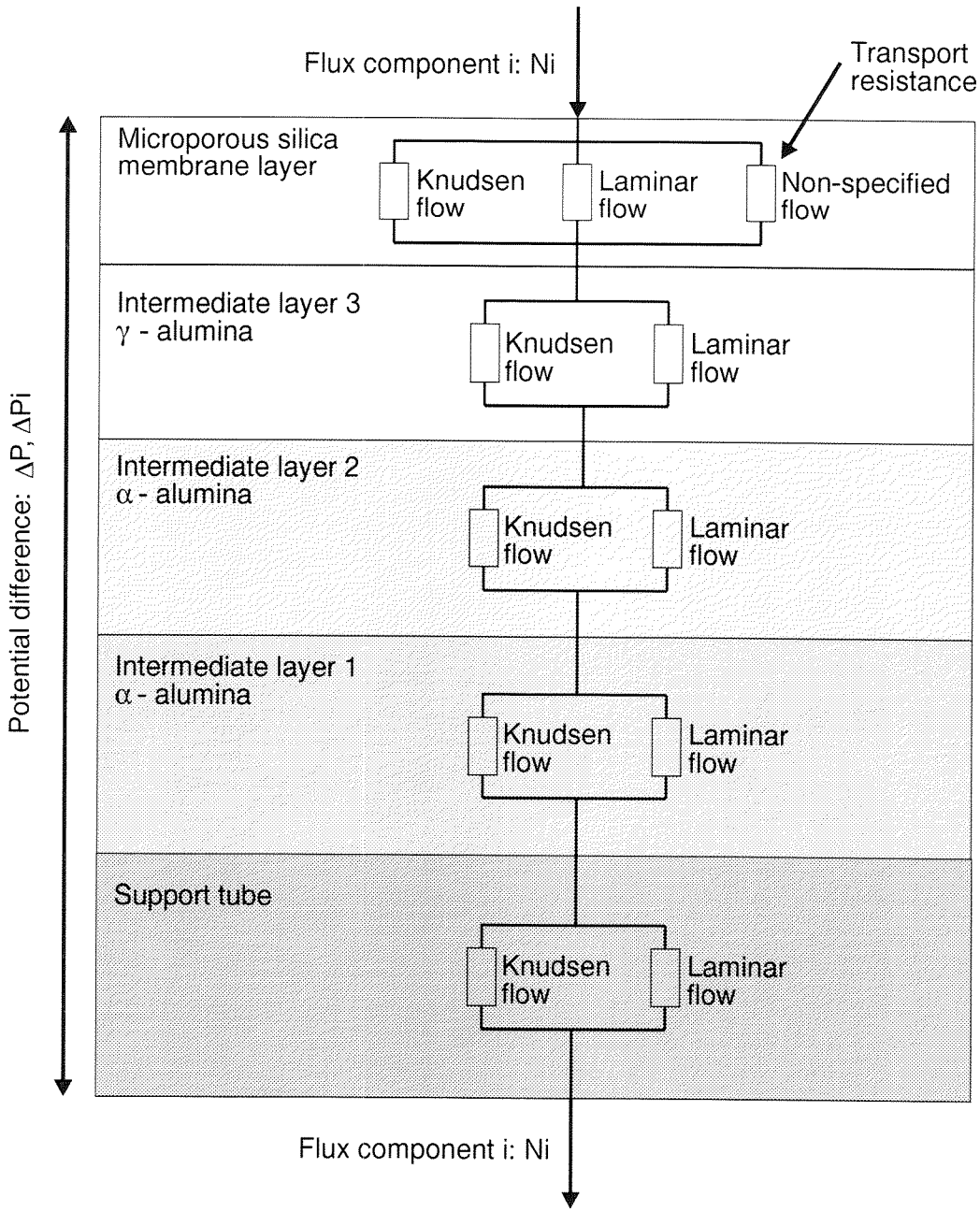
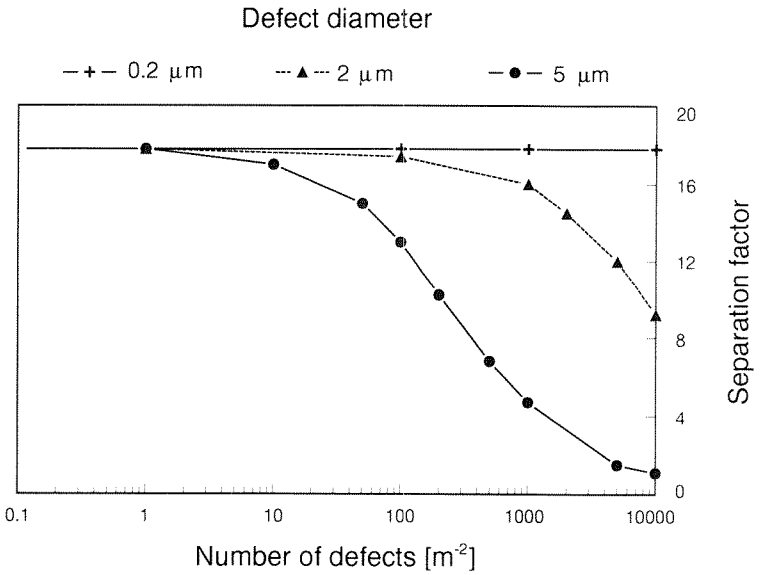


Figure 3 *Gas transport represented as an electric analogue circuit.*

the activated transport mechanism in the high-selective silica top layer (layer 5) is not well known, calculations were done presupposing some values for the gas permeabilities of this layer. Estimates for these values were based on our previous silica membrane measurements and those of Uhlhorn (Uhlhorn 1990). Details of the modelling will be published elsewhere.

A typical result of our calculations is given in figure 4. We see that if the H_2/CO_2-selectivity of the silica separation layer is assumed to be 25 for a mixture of 30%-H_2/70%-CO_2 and the H_2-permeance 10^{-7}mol/m^{2}sPa the separation factor drops significantly above a defect density of 100/m^2 for 5 µm diameter defects and above 1000/m^2 for 2 µm defects. The situation becomes more severe at the same selectivity when the permeancy decreases to 10^{-8}mol/m^{2}sPa. In table 1 the "allowed" defect densities in the separation layer for several defect sizes and silica coating permeancies are given when a decrease in separation factor of 10 % is allowed.



Figuur 4 *The detrimental influence of defects on the separation factor of the membrane.*

Table 1 *Allowed defect size and defect density for a maximum reduction of 10% of the separation factor at different permeancies of the membrane.*

Permeancy → Defect diameter ↓	10^{-6} mol/m^{2}sPa	10^{-7} mol/m^{2}sPa	10^{-8} mol/m^{2}sPa	10^{-10} mol/m^{2}sPa
5 µm	200	25	2	< 0.1
2 µm	8000	900	90	1
0.2 µm	ca. 100000	ca. 50000	ca. 20000	3000

5. TRANSLATION OF DEFECTS

Our working hypothesis that defects are translated from layer to layer, just as defects in a paint layer are often caused by irregularities on the surface to be painted, was already demonstrated in our former development work on the tubular Knudsen membranes (van Veen 1991). Such a system is in fact a hierarchical system. Other important reasons causing translation of defects or irregularities from the gamma alumina coating to the silica coating which can be added to the hypothesis are the following:

1. The minimum layer thickness at which the coating is continuous, is probably not much less than the critical layer thickness for cracking during drying and calcining. At lower thicknesses (say 50 nm) the layer becomes of the order of the grain size of the gamma alumina layer which determines the minimum achievable micro-roughness of this layer.
2. The wet visco-elastic gel layer during sol-gel coating is capillary unstable, because the contact angle is $\geq 10^{\circ}$. This means that irregularities in the substrate as pore defects can cause a hole in the gel layer.

Also there is the difficulty that defects as micro cracks and pinholes are not easily detected in a 100 nm thin silica membrane. So, on the basis of the above considerations and of the results in table 1 we simply assumed that if defects of 3 to 5 μm size are not allowed in the silica coating they are also not allowed in the gamma alumina Knudsen layer. So we had to increase the bubble point of our 80 cm long and 14 mm in diameter Knudsen diffusion membrane support tubes from 0.5 bar to at least 3 bar in water.

6. SUPPORT IMPROVEMENT

The break through (bubble point) pressure at which a non-wetting (gas) phase percolates a porous layer saturated with a wetting liquid is dependent of the void neck size in the ceramic coating (Dullien 1992). In the ideal case the void neck size distribution is determined by the random particle packing in the porous ceramic coating. However, in the case of defects (i.e. voids in the packing not caused by unavoidable (stochastic) packing "faults", but by voids originating from aggregates, pinholes, micro cracks and dust), this void population is largely independent from that originating from the particle packing and is superponed on the random particle packing void distribution. The defect void distribution causes the low bubble point in the classical Knudsen membrane system in our opinion.

We have found that the support system can be improved significantly with respect to the bubble point when:

1. An extra intermediate macroporous alpha alumina layer was introduced by the same filmcoating procedure reported earlier by us (van 't Veen 1992).
2. The thickness of the alpha alumina coatings was increased to approximately 50 µm.
3. The coating suspensions were completely free from aggregates and agglomerates.

The bubble point pressure appeared to be dependent on the layer thickness of the coating. This shows that the coating does not behave as a bulk porous medium. The bubble point of a macroporous support tube coated with two alpha alumina layers has shown to be at least 3 bar and the pore radius of the final alpha alumina layer is 80 nm with the surface having a mirror like appearance. Application of a 3 µm thick gamma alumina coating by colloidal filtration does not increase the bubble point very much. But the defect density reduces and the surface becomes even more smooth. The increased improvement of the support with the subsequent layers can be seen clearly in figure 5. In this figure the bubble point and bubble defect density are given as a function of the pressure for the various situations.

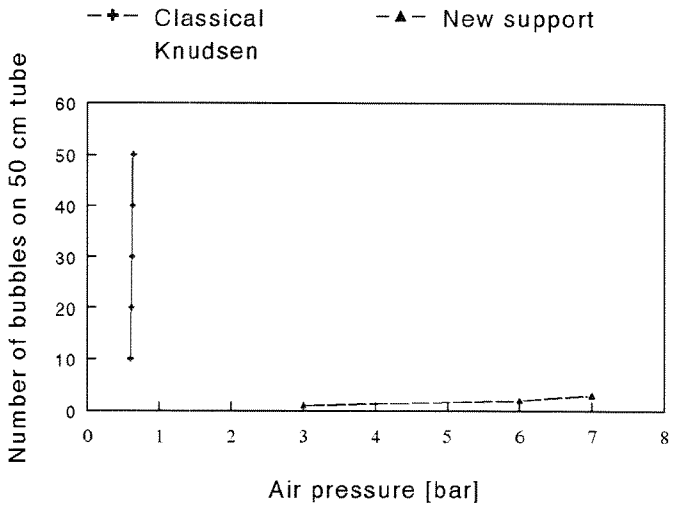


Figure 5 *Bubble test graph of 'Classical' Knudsen membrane and new high selective membrane support.*

Now, we are convinced to have a support, consisting of 3 layers on a tube, that is suitable for the successful development of a high-selective gas separation coating on top of it.

The resistance to gas transport of the complete multi layer support system is negligible compared to that of high selective separation layers with low permeability. In UF liquid applications such a support system gives an undesired flux decline, but in that case our classical three layer system will suffice. Also we point out that due to the filmcoat method we use (van 't Veen 1992) extra interfacial resistances are avoided because there is no layer interpenetration as can occur with slip casting.

7. FUTURE WORK

Work is being done concerning the optimisation of high-selective silica membranes towards selectivity and permeability. The membranes are tested under realistic gas mixture (incl. water), gas flow, pressure, and temperature conditions. Furthermore their long time stability is monitored by exposing them to real application conditions and intermittent in-situ permeation measurements. Stability improvement of silica membranes and development of other microporous high selective membrane materials, for which intrinsically a higher stability is envisaged, are also subject of research.
High-selective silica membrane tubes with a length of 80 cm and single tube joining techniques which operate reliably under e.g. realistic coal gas conditions are available and work is being carried out towards the development of high surface area/low cost support systems with the same quality as our present support tubes.

8. ECN GAS SEPARATION GROUP

The ECN Gas Separation Group is currently consisting of Peter T. Alderliesten (team leader) Ben C. Bonekamp, Paul J.A.M. Blankenvoorde, Maarten Bracht, Albert J.G. Engel, Charles W.R. Engelen, Wim F. van Leeuwen, Jack A.J. Peters, Paul P.A.C. Pex, André Roskam, Henk M. van Veen and W. Hans van 't Veen.

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