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PERMSELECTIVITY CHARACTERISTICS OF SUPPORTED CERAMIC ALUMINA MEMBRANES

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ABSTRACT

Supported gamma-Al_2O_3 ceramic membranes have been prepared by sol-gel techniques from alkoxide precursors. Permeability and rejection characteristics of these membranes have been used to determine the effect of sol concentration on membrane thickness. Rejection coefficients of poylethyleneglycols of different molecular weights and of several protein streams of possible industrial interest were also determined. Permeabilities were also measured for several feedstocks. Initial studies of protocols for regenerating membranes have been carried out.

INTRODUCTION

During the past two decades the use of membranes in separation processes has grown more frequent. In industry, membranes have been employed in reverse osmosis, ultrafiltration, and electrodialysis to concentrate and fractionate both liquid and gaseous process streams. The advantages associated with the use of membranes include high permselectivities, low

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energy requirements compared to other separation methods, and operation at the low temperatures necessary to avoid degradation of pharmaceuticals and foodstuffs. Since the midsixties, polymeric membranes have been employed with the greatest success; however, ceramic membranes are now generating significant interest.

Ceramic membranes have many advantages over their polymeric counterparts, particularly with respect to their durability. Ceramic membranes have the ability to withstand exposure to high temperatures and harsh chemicals (conditions often necessary for the cleaning of membranes in pharmaceutical and foodstuff applications). Therefore, many research groups are currently investigating the development of permselective ceramic membranes. The present paper describes the results of some of our efforts to utilize sol-gel technology to prepare permselective ceramic membranes and to test their potential for industrial applications.

Many different preparative methods have been used to fabricate both unsupported and supported ceramic membranes formed from Al_2O_3 (1-11). Our research program is directed toward producing ceramic membranes of gamma-Al_2O_3 for possible adaptation to industrial processes. Our major objectives are : 1) to develop techniques for the fabrication of these membranes that optimize permselectivity and permeability; 2) to develop permselective membranes useful in processing streams of practical industrial interest and 3) to test these membranes using such streams as feedstocks under realistic processing conditions. Our earlier effort in this area (13) focused on the physio-chemical properties of these membranes. The present paper concerns the application of these membranes to selected test streams.

MATERIALS

Aluminum tri-sec-butoxide was obtained from Alfa Chemical Company. Both ethyl alcohol (absolute) and isopropanol were AR grade. All chemicals were used without further purification. Water used in reactions was deionized using a Milli-Q water purification system (Millipore Corp.).

The clays used in the preparation of the membrane supports were obtained from Minnesota/Midwest Clay Company (see Table 1 for information relevant to the characteristics of these clays).

Table 1. Compositions of Clays Used to Prepare Membrane Supports (Weight Percentages)

Component	'OM-4' Ball Clay	'AP-Green' Fire Clay
SiO_2	55.6	55.23
Al_2O_3	28.6	38.11
TiO_2	1.8	2.05
Fe_2O_3	1.0	1.55
CaO	0.1	0.32
MgO	0.4	0.71
Na_2O	0.1	0.16
K_2O	1.1	1.45
Ignition Loss	11.4	10.0
Bulk Density	0.62 (g/cc)	1.26 (g/cc)

The polyethylene glycols used in the permselectivity studies were obtained from Aldrich Chemical Company. Their nominal molecular weights were 200, 600, 1000, 2000, and 8000. The 98-99% pure bovine serum albumin was purchased from Sigma Chemical Company. The acid cheese whey used was obtained from the University of Wisconsin Dairy plant; it was produced during their manufacture of cottage cheese.

METHODS FOR PRODUCTION OF MEMBRANES

The Al_2O_3 membranes were prepared using the sol-gel technique described in a previous paper (12). The experimental protocol is summarized in Figure 1. The indicated approach yielded gamma-Al_2O_3 membranes from particulate gamma-AlOOH sols.

ANALYTICAL METHODS

Polyethylene glycol and bovine serum albumin. The aqueous solutions of PEG and bovine serum albumin were analyzed by total organic carbon analyses using a Xertex DC-80 automated laboratory total organic carbon analyzer (TOC).

Cheese whey protein. Protein analyses of the cheese whey were carried out using the Kjeldahl method for total nitrogen and non-protein nitrogen. The analyses were carried out using a Tecator 1015 digester and a Tecator 1026 distilling unit.

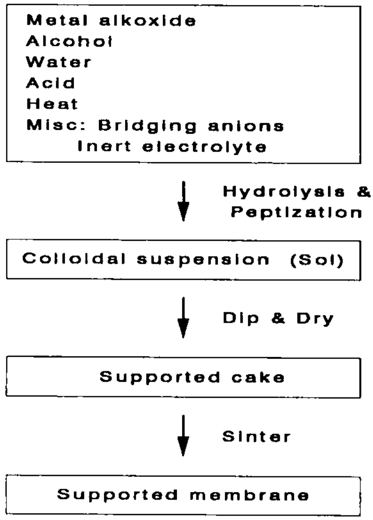

Figure 1. Preparation protocol

Cheese whey total solids. Total solids analyses of the cheese whey were determined by the gravimetric method of the AOAC.

Equipment. The apparatus used to determine the permselectivity characteristics of the ceramic membranes was a standard test loop (see Figure 2) which consisted of the following components: feed cylinder, LEWA positive displacement pump with outlet flow dampener, high pressure relief valve, 20.6 mm I.D. by 22 cm-long pressure cell or 20.6 mm I.D. by 42 cm-long pressure cell, needle valve, back pressure regulator (for high corrosion service), Tescom Model 26-3225-24 springloaded back pressure regulator (for low corrosion service), retentate flow rotameter, permeate collector, and tubing coil inside a water bath (for recycled retentate/feed temperature control).

The pressure cell housed a test-tube shaped supported membrane. Cajon fittings allowed a rubber O-ring to be compressed against both the supported membrane and the housing. The fittings resulted in a pressure-tight isolation of the feed (high pressure) and permeate (low pressure) streams.

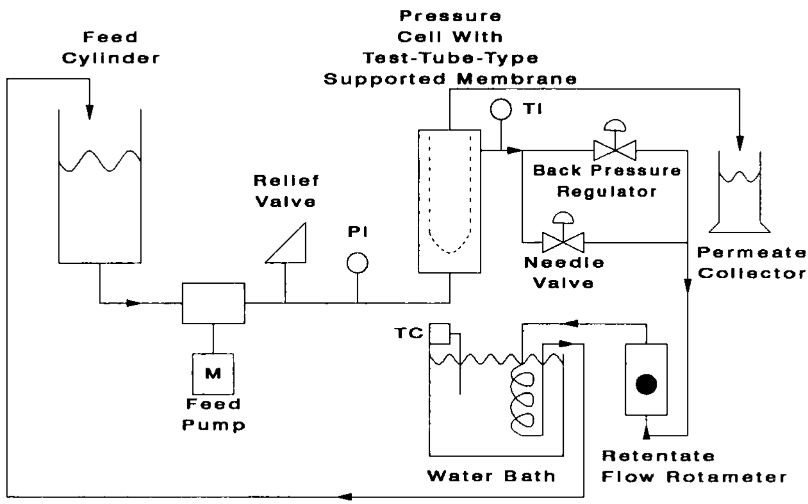

Figure 2. Schematic diagram of permeability test apparatus.

The membranes were thermally regenerated in a Lindberg laboratory box furnace, model 51828.

RESULTS AND DISCUSSION

Sol concentration effects

Permeation rate and rejection measurements were conducted for a series of supported Al_2O_3 membranes. The initial alkoxide sol from which these membranes were cast had the following composition:

0.5 M Total Al
0.035 M NO_3^-
pH 3.9-4.0

From this sol three further sols were made by concentrating the sol by factors of 1.5, 2.0 and 3.0 times by weight. This concentration was accomplished by allowing the water to evaporate slowly from the sol. The membranes were made by dipping water soaked supports into the sols and then drying them (see Fig.1). They were fired after from 1 to 4 dips. This sequence was repeated three times.

Evidence that the membrane thickness increased with concentration was provided by checking the permeability of the supported membranes to pure water. A mathematical analysis of the dipping procedure indicates that for equal draining times the thickness of the layer which adheres to the support should be proportional to the viscosity of the fluid into which the support is dipped. For the alkoxide sols of interest, the viscosity is proportional to the concentration of the sol. Since the permeability of a supported membrane decreases with increasing thickness of the membrane proper, higher permeabilities indicate thinner membranes. This reasoning indicates that a plot of permeability versus sol concentration should indicate that the permeability decreases with increasing concentration of the sol used in fabrication of the membrane. Figure 3 contains such plots for a fixed number of dips per firing. For one and two dips per firing the permeabilities of the supported membranes decrease dramatically as the concentration of the sol is increased. It should also be noted that it was impractical to test any of the membranes formed from sols which had been concentrated by a factor of 3.0 because these membranes were so thick after only a single dipping that they cracked and flaked off during

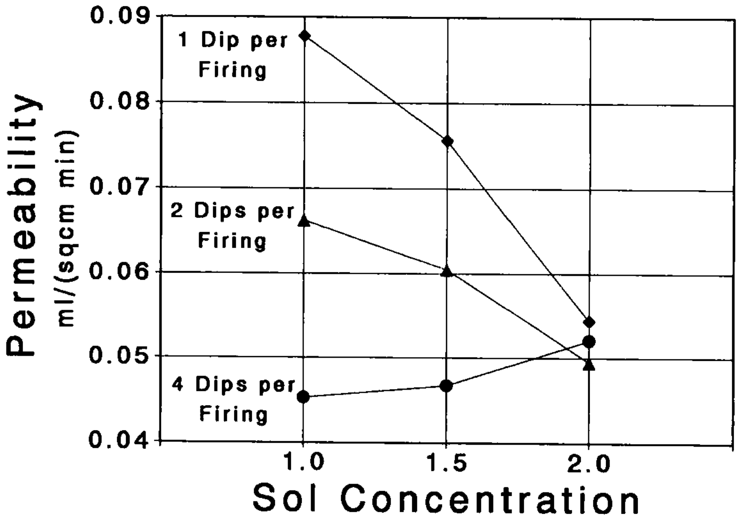

Figure 3. Permeability at 100 psi and 25°C versus sol concentration with dips/firing as a parameter.

the drying step of the preparation protocol. We believe that the fact that the expected trend is not observed in the data for 4 dips per firing can be attributed to the possibility that cracks may begin to develop in these thick membranes due to stresses induced during the drying and firing steps of the protocol.

Further evidence in support of the working hypothesis that the thickness of the supported membrane increases with increasing sol concentration is provided by data for the rejection of polyethyleneglycol (PEG) with an average molecular weight of 1000. For a conventional filtration model, rejection should be strongly related to the thickness of the membrane. Thus a plot of rejection versus concentration should show rejection increasing with sol concentration. Figure 4 contains such plots. The data indicate that as the sol concentration increases, the rejection increases for those membranes prepared using one or two dips per firing. However, the data show an opposite trend when 4 dips per firing were employed. One can again interpret these data as indicating a pathological condition in which cracks are present in the membrane. The data introduced thus far indicate that in addition to the concentration of the sol, the number of dips per firing has a significant effect on the permselectivity

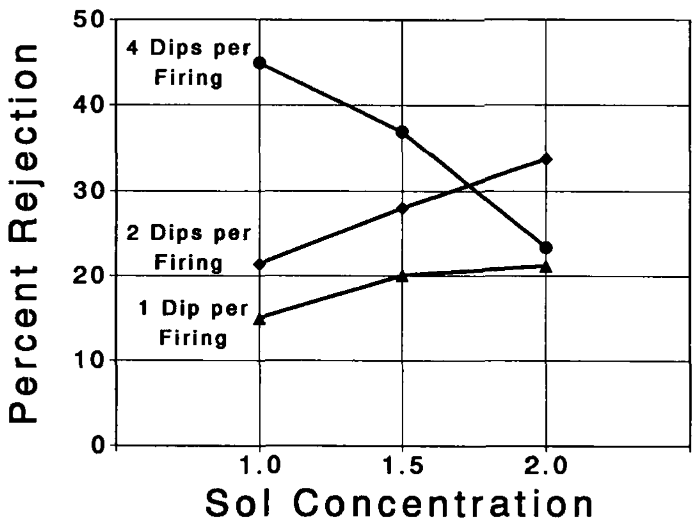

Figure 4. Rejection of 1000 MW PEG for supported alumina membranes vs sol concentration.

characteristics, and thus the thickness of the membrane. Inspection of the data in Figures 3 and 4 indicates that for the membranes prepared from the unconcentrated sol and the sol concentrated by a factor of 1.5, the permeability decreases and the rejection increases as the number of dips per firing increases. For those membranes prepared from the sols concentrated by a factor of 2.0, the unanticipated results can again be interpreted in terms of a much greater propensity of the supported membranes to contain cracks when 4 dips/firing are utilized in their fabrication.

<u>Permselectivity Measurements</u>

In order to characterize supported Al_2O_3 membranes various aqueous test streams were used. The initial alkoxide sol from which these membranes were cast had the same composition as the precursor sol from which the concentrated sols described in the previous section were produced. The membranes were fabricated using the same protocol and were fired after every 4 dips. The sequence was repeated three times (yielding a total of 12 dips). Solutions of polyethylene glycol (1% w/w, molecular weights of 200, 600, 1000, 2000, and 8000), cheese whey, and bovine serum albumin were used. The test loop was operated with total recycle of retentate and permeate streams so as to maintain a constant composition of the feed stream. Solute rejections were calculated as

$$\text{Percent Rejection} = 100(1-[C_{permeate}/C_{feed}])$$

Rejection data for feedstocks of varying molecular weights should show an increase in rejection with increasing molecular weight. Theoretically, the larger the molecule is, the more resistance there will be to its passage through the membrane. Hence higher rejection coefficients should be observed for larger molecules. Figure 5 contains a plot of data which indicates that the rejection coefficients for alumina membranes increase with increasing molecular weight, as expected. These data indicate that the molecular weight cutoff of the alumina membranes is approximately 2000. In conventional practice the molecular weight cutoff is defined as corresponding to 80% rejection. Figure 5 also contains data which permit one to compare the characteristics of these alumina membranes with those of alumina and zirconia membranes being developed by Alcoa.

Potential applications for these membranes include the recovery of proteins from food product waste

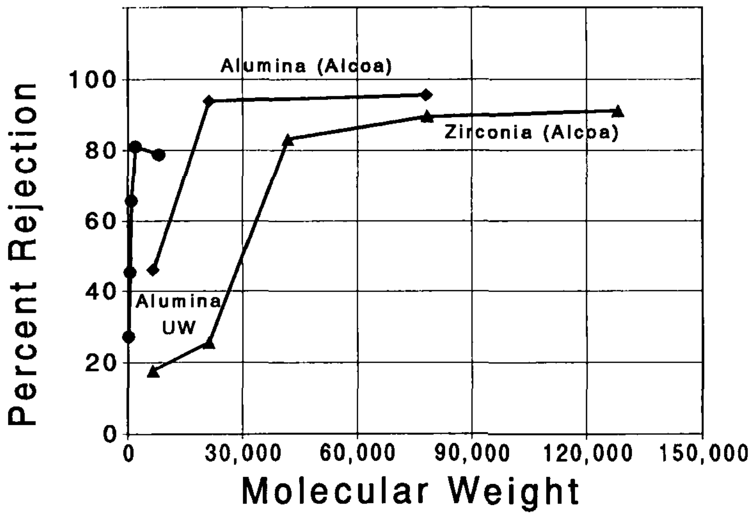

Figure 5. Rejection for supported alumina membranes vs molecular weight.

streams. Given the size of these proteins, the rejection coefficients of these species are expected to be nearly 100%. Data for experiments on the proteins from cottage cheese whey and bovine serum albumin are shown in Figure 6 along with those for 1000 MW PEG samples. As expected, values of the rejection coefficients lie between 95% and 100%. (The error in the analysis technique is larger than the deviation from 100%). Also shown are data characterizing the total solids rejection obtained when cottage cheese whey is used as the process fluid.

<u>Permeability Measurements</u>

In order to further characterize the supported Al_2O_3 membranes, permeabilities of various test streams were determined. The same solutions and membranes used for permselectivity measurements were used. Permeability measurements involved recording the time necessary to collect a given amount of fluid at a constant pressure drop across the supported membrane. Permeability was calculated as

Permeability = vol / (area * time * pressure drop)

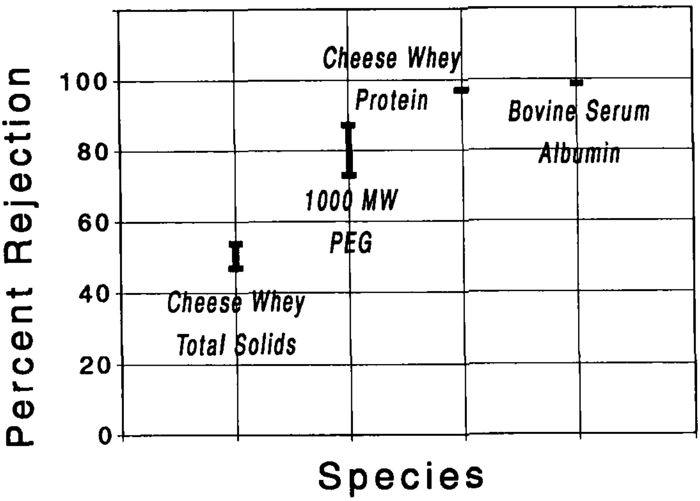

Figure 6. Rejection for supported alumina membranes by species.

The results of these experiments are summarized in Figure 7. It should be noted that for the cheese whey tests the system was operated at 40 C while the other experiments were conducted at ambient temperature. The use of a higher temperature for the cheese whey was necessary to avoid excessive fouling that occurred at lower temperatures. This fouling also accounts for the significantly lower permeability of the cheese whey. We attribute the fouling to inadequate clarification of the whey prior to use. For mechanically stable systems, it is usually assumed that permeability is independent of pressure. A simple experiment can be devised to test this hypothesis for our system. Figure 8 contains a plot of data for Al_2O_3 membranes. The plot indicates that the permeability of these membranes is slightly dependent on pressure, the permeability increasing with increasing pressure.

Regeneration

An essential step in the development of a membrane for commercial sale is the ability to develop a cleaning or regeneration procedure. Currently only one

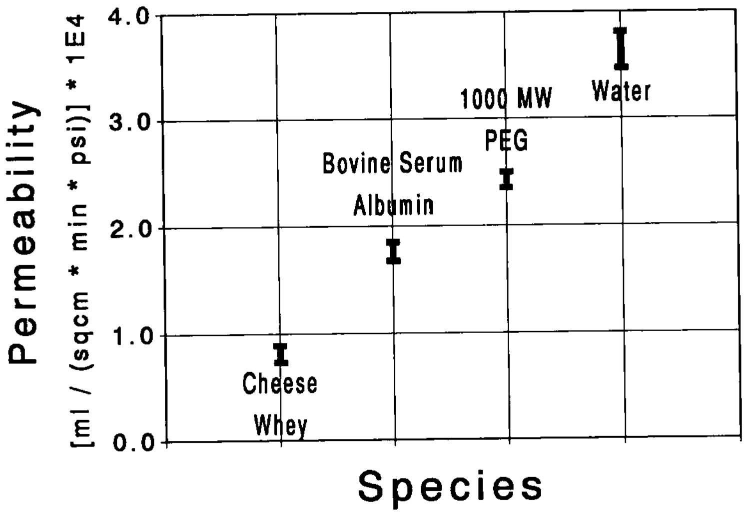

Figure 7. Permeability at 100 psi and 25°C for supported alumina membranes by test streams

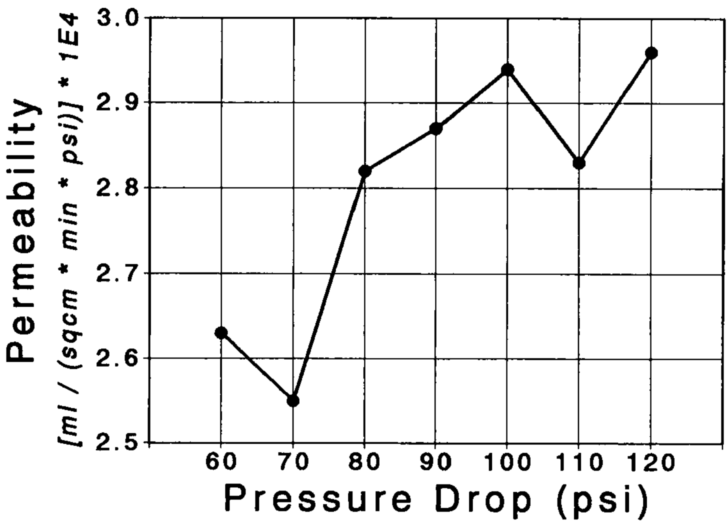

Figure 8. Permeability at 25°C for supported alumina membranes vs pressure drop across the membrane.

method of regeneration of these membranes has been tested. Membranes were fouled excessively with cheese whey and then cleaned. Cleaning consisted of washing the membrane with water and then heating the membrane to 500 C for 1 hour. This process met with limited success. From 50 to 75 percent of the original water permeability was retained after 2 regenerations. Despite this loss in permeability, however, the membranes were still able to reject in excess of 95 percent of the cheese whey protein. Chemical and mixed thermo-chemical regeneration processes are now being explored.

SUMMARY

Permselectivity and permeability measurements were used to characterize supported Al_2O_3 membranes. Such measurements can be used to optimize the experimental protocols used to prepare membranes with optimal permselectivity. They can also be used to optimize the conditions under which the membranes are used. We have been able to produce membranes that reject essentially 100% of the solutes contained in test streams of interest to industry. Our results to date have been very promising and we are currently investigating additional steams of industrial interest. Further modifications of the experimental protocols to possibly include the use of other ceramic systems, particularly titania, are also being investigated. The long range goal of this project involves the testing of these membranes for industrial applications and the improvement of the experimental protocol involved in their fabrication so as to optimize permselectivity and permeability.

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