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Physicochemical Properties of Supported γ-Al_2O_3 and TiO_2 Ceramic Membranes

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Abstract

Supported γ-Al_2O_3 and TiO_2 ceramic membranes were prepared by sol-gel techniques from alkoxide precursors. Tests were conducted to measure the permeabilities of these membranes to solvent under a variety of operating conditions. Variables studied were feed temperature, length of time on stream, and feed pH. The stabilities of the membranes in harsh chemical environments were also determined. An alternative method for preparing supported ceramic membranes is also suggested.

INTRODUCTION

Over the past two decades membrane separation processes have been applied with increasing frequency to solve separation problems. Industry has utilized such techniques as reverse osmosis, ultrafiltration, and

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electrodialysis to effect the concentration and fractionation of a wide variety of process fluids, both liquid and gas. Major advantages associated with the use of these processes include high permselectivities, low energy requirements relative to alternative separation techniques, and suitability for operation at low temperatures in processing such thermally labile materials as pharmaceuticals and foodstuffs. Throughout the time frame in question, systems based on polymeric membranes have dominated the commercial market, but significant interest curently exists in developing ceramic-based systems for industrial-scale applications.

There are several potential advantages to the use of ceramic membranes, particularly with respect to their stability at high temperatures, in harsh chemical environments (e.g., in strong cleaning solutions or in the presence of organic solvents), and in the presence of microbes. Consequently a number of research groups are actively pursuing the task of developing permselective ceramic membranes. Previous papers (*1*, *2*) have described the results of some of our efforts to utilize sol-gel technology to prepare permselective ceramic membranes and to characterize some of their fundamental properties. This work focuses on some of the novel permeation properties observed with ceramic TiO_2 and γ-Al_2O_3 membrane systems. These properties relate largely to the chemical and physical nature of the membrane surfaces.

MATERIALS AND METHODS

Materials

Titanium tetraisopropoxide was obtained from Aldrich Chemical Company while aluminum tri-*sec*-butoxide was obtained from Alfa Chemical Company. Ethyl alcohol (absolute), isopropanol, sodium perchlorate, perchloric acid, and sodium hydroxide were AR grade. All chemicals were used without further purification. Water used in the reactions was deionized using a Milli-Q water purification system (Millipore Corp.).

Clays used in the preparation of membrane supports were obtained from Paoli Clay Company and had the compositions given in Table 1.

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	55.2
Al_2O_3	28.6	38.1
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
Loss on ignition	11.4	10.0
Bulk density (g/cm^3)	0.62	1.26

Methods for Production of Membranes

The TiO_2 and Al_2O_3 membranes were prepared using the sol-gel technique described in a previous paper (*1*). The experimental protocol is summarized in Fig. 1. The indicated approaches yielded TiO_2 and γ-

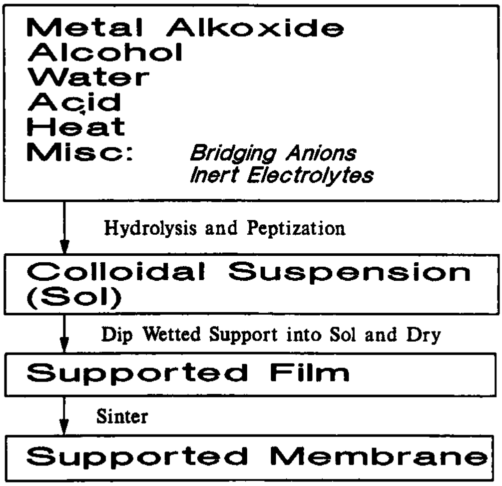

FIG. 1. Protocol for preparation of supported membranes.

Al_2O_3 membranes from both particulate and polymeric $Ti(OH)_4$ sols and particulate γ-AlOOH sols.

Analytical Methods

pH. Hydrogen ion concentrations were determined using an Orion Research (Boston, Massachusetts) Model No. 81-72 electrode with a Model No. 701A meter.

Equipment. The apparatus used to determine the permselectivity characteristics of the ceramic membranes was a standard test loop which consisted of the following components (see Fig. 2): feed cylinder, American LEWA HL-1 positive displacement pump with outlet flow dampener, high pressure relief valve, 20.6 mm i.d. by 22 cm-long pressure cell, needle valve backpressure regulator (for high corrosion service), Tescom Model 26-3225-24 spring-loaded backpressure regulator (for low corrosion service), retentate flow rotameter, permeate collector, and stainless steel tubing coil inside an MGW Lauda RC20 Model T-2 water bath (for recycled retentate/feed temperature control).

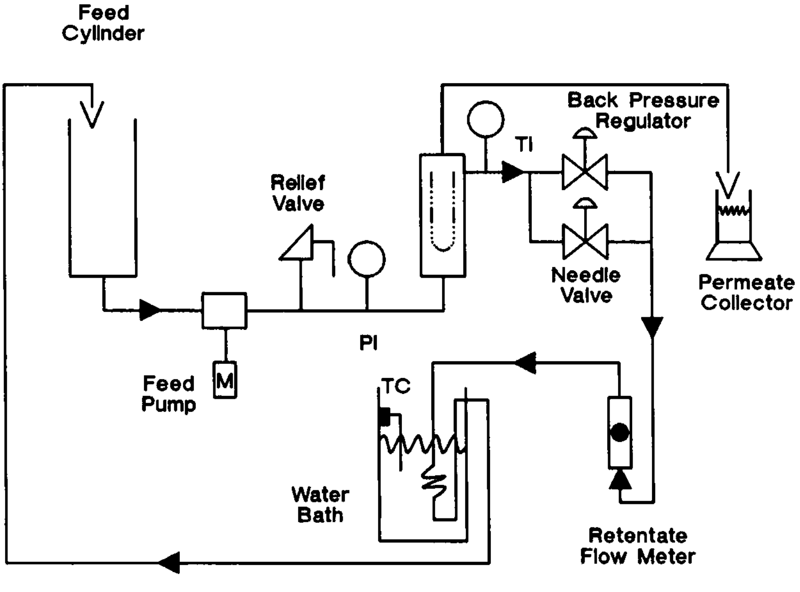

FIG. 2. Schematic diagram of permeability test apparatus.

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.

RESULTS AND DISCUSSION

Permeability Measurements

Permeation rate measurements were conducted for various supported Al_2O_3 and TiO_2 membranes. The sols used to prepare the membranes had the following compositions:

Alumina Sol	Titania Sol
0.5 *M* total Al	0.93 *M* total Ti
0.035 *M* NO_3^-	0.111 *M* NO_3^-
10^{-5} *M* H_3PO_4	
pH 3.9–4.0	pH 1.3

Water-soaked dry supports were dipped into the sols and dried 8 times using the procedure shown in Fig. 1. They were fired after the fourth and eighth dips in order to fix the membrane in place. Electron photomicrographs of the resulting supported membranes suggested that the membrane layers were about 1 μm thick.

Dipping Time

Leenaars (*3*) noted previously that varying the length of time a dry support was dipped into an alkoxide sol changed the amount of membrane deposited onto the support. In his case this result was due to capillary forces in the pores of the support. The procedure used in this study employed dipping onto a wetted support; hence capillary effects were expected to be negligible. However, this variable could not be dismissed arbitrarily, and therefore an experiment was conducted to observe the effect of dipping time on the resulting increase in membrane resistance.

TABLE 2
Effect of Dipping Time on Membrane Permeability

Time of dipping (s)	Flow rate before dipping ($cm^3/cm^2 \cdot min$)[a]	Flow rate after dipping ($cm^3/cm^2 \cdot min$)[a]	Loss in permeability (%)
20	0.265	0.202	23.7
200	0.238	0.191	19.6
2,000	0.257	0.199	22.6
20,000	0.238	0.147	38.3

[a] At 25°C and 100 psig for pure water feed.

Supports with similar permeabilities were dipped into an alumina sol once for various amounts of time, then dried and fired to 500°C. Since the supports were wetted prior to dipping, it was felt that the dipping time should be of minor consequence, there being no capillary action involved as in the case of a dry support. Thus, for an unagitated dipping any differences in membrane permeability should have resulted only from diffusion of the sol into the water contained within the pores of the support. From the data in Table 2 it can be seen that only at the highest dipping time did diffusion become significant enough to alter the effective membrane permeability. The lack of dependence of the resistance of the membrane on the dipping time facilitates the development of an experimental protocol for fabricating membranes with reproducible properties.

Feed Temperature

It has been noted previously (*4*, *5*) that the permeabilities of polymeric membranes vary with temperature in a manner which is of the Arrhenius form:

$$J = J_0 \exp(-E/(RT))$$

To determine if this type of behavior is also characteristic of ceramic membranes, permeability measurements for a pure water feed were carried out using alumina and titania supported membranes. If the Arrhenius relation is obeyed, a plot of $\ln J$ versus $1/T$ should be linear. Figure 3 demonstrates that for the temperature range of 7 to 40° C the Arrhenius relation is indeed obeyed. However, the high-temperature data appear to fall slightly below the expected values. These data were

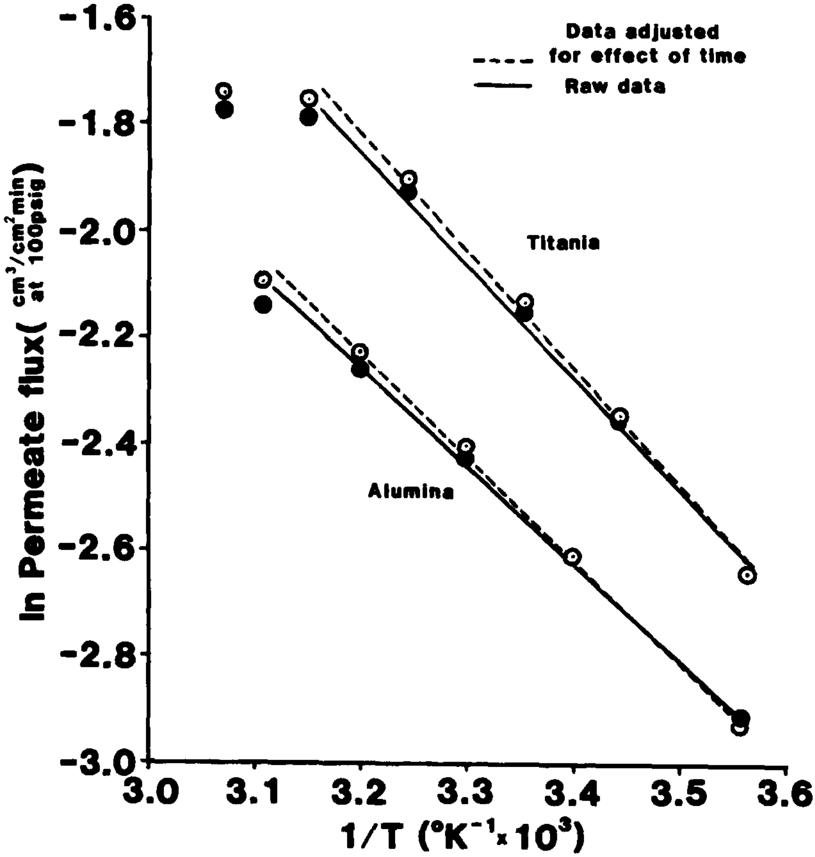

FIG. 3. Effect of feed temperature on permeability.

probably affected by vaporization and recondensation of permeate onto the permeate outlet line of the test apparatus.

From the linear portions of the plots, the slopes yield values of about 4000 and 3600 cal/g·mol for the activation energies of water transport through titania and alumina membranes, respectively. These values are comparable to, but slightly lower than, those observed for polymeric membranes (*4*, *5*).

Time On-Stream. Ceramic membranes can carry a surface charge. For this reason it was felt that the membrane surfaces might hydrate in the presence of water, and that this hydration might effectively restrict permeation rates through the pore structure of the membrane. Hydration of metal oxide surfaces has been observed previously (*6*, *7*).

This concept was tested on groups of supports which had been dipped 8 times into either 0.93 *M* titania or 0.50 *M* alumina sols, then fired according to established procedures. The resulting supported membranes were checked for permeability to pure water after having been kept dry prior to testing. The permeabilities of the membranes to water were checked over a period of several days. Between measurements, the supported membranes were stored in pure water. Except for the initial test, the membranes were wet when installed in the flow measuring apparatus.

The data in Fig. 4 demonstrate that the permeabilities of these membranes declined as time elapsed. Of note is the fact that the loss in permeate flux was found to be much greater during the time the flows were being measured. Thus, forced contacting of water with the membranes appears to be much more "efficient" than stagnant contacting in altering the charge characteristics of the membrane surface. The data are replotted in Fig. 5. This plot takes into account only the time that there was forced flow through the membrane. A permeability loss of about 3.3% of the original flow was observed for the initial 10 to 12 h on-stream,

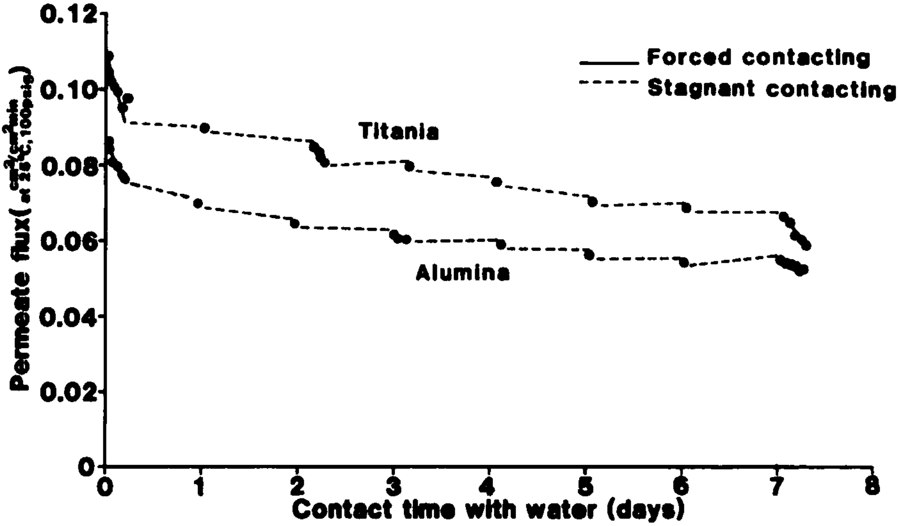

FIG. 4. Decline of permeate flux with contact time.

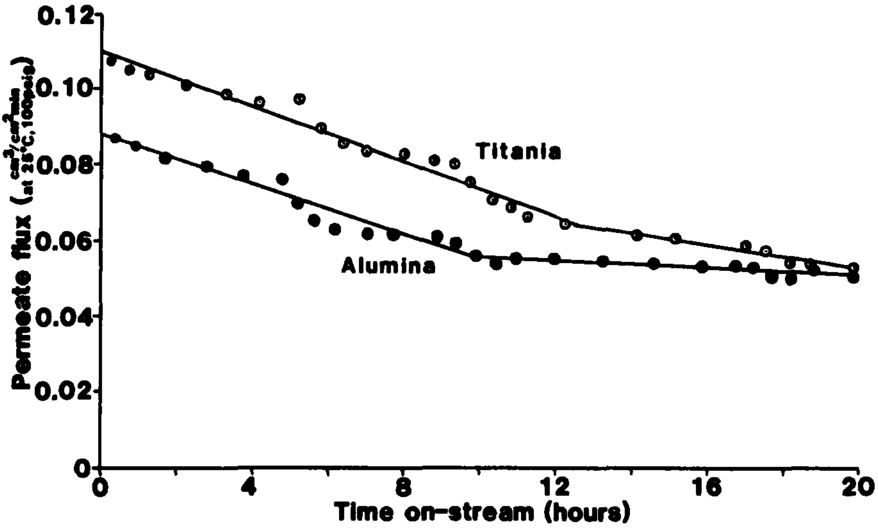

FIG. 5. Decline of permeate flux with time on-stream.

followed by decays of 0.4 and 1.4%/h for the alumina and titania supported membranes, respectively. (A subsequent test with a clay support on which no membrane was supported demonstrated that no loss of permeability could be attributed to the macroscopic pores of the clay.) These tests were conducted at 25°C. However, a 7-h experiment conducted at 50°C with the same alumina membrane gave virtually the same rate of flux decline.

This loss of permeability has practical implications from the point of view of industrial efficiency. If the permeability declines as a result of hydration effects, then it should be possible to regenerate the supported membranes by drying. To test this hypothesis, the hydrated supported membranes were dried according to the following procedure: 1) drying for 15 min at 60°C to remove unbound water, 2) heating over a 15-min period to the desired drying temperature, 3) drying for 1 h at the maximum drying temperature, and 4) cooling over a 15-min period back to room temperature. All drying was conducted in dry air ovens without forced circulation. It was assumed that the above procedure allowed for expedient regeneration while imposing minimal thermal stresses on the membranes.

Hydrated supported titania membranes were fully regenerated using the above procedure with an ultimate drying temperature of 300°C.

Hydrated supported alumina membranes required drying temperatures of ~350–400°C to recover fully their permeabilities.

Feed pH. Because the ceramic membranes are comprised of ionic species and can bear a surface charge, it was felt that the permeabilities of these microporous filtering media might be pH-dependent. To test this hypothesis, the permeabilities of the supported membranes to 0.01 *M* $NaClO_4$ solutions of various pH values were measured. The initial feed was a 0.01 *M* $NaClO_4$ solution whose pH had not been adjusted. The membrane was stored in this solution for 24 h prior to the test in order to equilibrate it with the solution. Due to the length of the experiments they were split into separate high and low pH runs for each membrane. Permeation rate measurements were taken until the permeate flow was determined to have reached an asymptotic value. Then the pH of the feed stream was altered and a new steady state approached. Following each set of runs the membranes were flushed with (deionized) water for 20 min, then dried overnight at 60°C prior to being equilibrated with the 0.01 *M* $NaClO_4$ solution for the subsequent experiment. Following the pH dependence studies, flux rates were again determined for a 0.01 *M* $NaClO_4$ solution whose pH had not been adjusted.

Plots of permeate flow loss relative to water feed, observed for $NaClO_4$ solutions at various pH values, demonstrated a clear dependence on pH for both the alumina (Fig. 6) and titania (Fig. 7) membranes. Of particular interest is the fact that alumina appeared to have maximum permeability at about pH 8–10, while the maximum permeability for titania was at a pH of ~4. Since these pH values roughly correspond to the isoelectric points of the membranes, this result was not surprising. At the isoelectric points, the membranes should bear a minimum charge. Under such conditions there will be less hydration of the pore walls, hence higher permeation rates should result. Moreover, the loss of permeability was more dramatic at pH values above the isoelectric point than below. One possible explanation for this result is as follows: If the pore wall is negatively charged (for the high pH case), then the wall will attract positively charged ions. These cations are known to hydrate more extensively than do anions. Hence the effect may be to extend the apparent restriction of the wall.

The permeation rate may also depend on the thickness of the Gouy-Chapman electric "double-layer" (*8*) and the streaming potential (*9*). These quantities are dependent on the ionic strength and ionic composition of the feed solution.

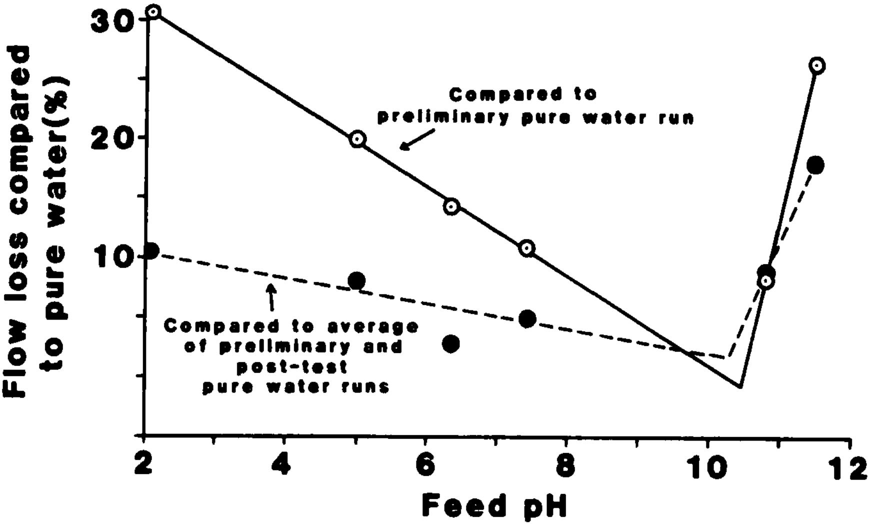

FIG. 6. Permeate flow loss vs feed pH; supported alumina membrane.

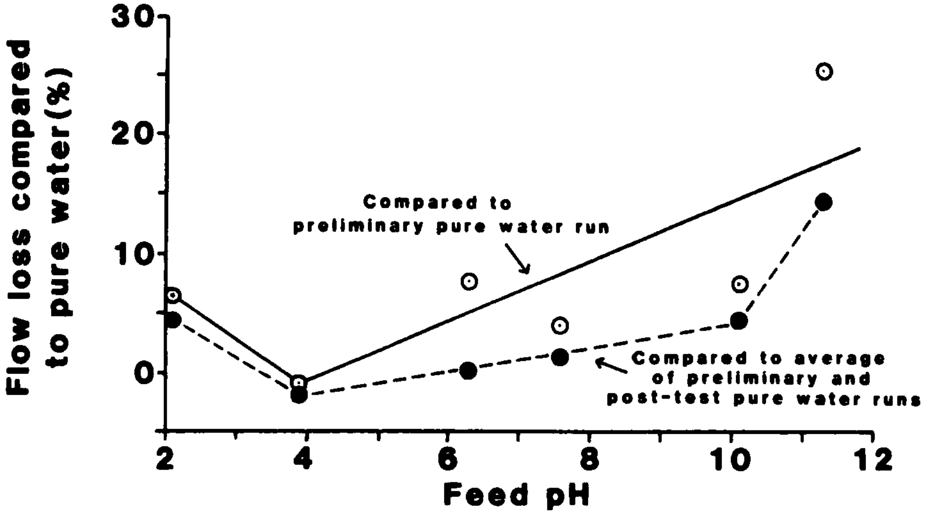

FIG. 7. Permeate flow loss vs feed pH; supported titania membrane.

Chemical Stability of Ceramic Membranes

To ascertain if the ceramic membranes would withstand harsh chemical environments, supported and unsupported alumina and titania membranes, and clay support material, were placed in aqueous solutions of varying hydrogen ion concentrations for 10 weeks. Degradation of the supported membranes was inferred by comparing the membrane permeabilities before and after the test period. Dissolution of unsupported membranes and clay support material was measured by analyzing for the amount of soluble metals in the solutions following the test period. The precise procedure is described below.

A. Supported Membranes

1. A number of supported alumina and titania membranes with surface areas ranging from 11 to 24 cm^2 were prepared according to the standard procedures discussed earlier. Permeabilities to water were measured after 0, 4, and 8 dips into the sol.
2. The supported membranes were placed in 500 mL aqueous 0.1 *M* $NaClO_4$ solutions and kept at room temperature (about 22°C) and in the dark in polypropylene containers. Initial solution pH values of 2.0, 3.5, 6.3, 8.4, 9.9, and 12.0 were used. The desired pH values were obtained by the addition of $HClO_4$ or NaOH. The solutions were considered to be saturated in atmospheric gases.
3. The pH values of the solutions were periodically measured and the pH adjusted as necessary to maintain a desired pH range (the pH adjustment was required only for solutions with original values of 8.4 and 9.9). Buffered solutions were not employed. This approach eliminated the possibility of adsorption of buffering chemicals on the oxide membranes.
4. The solutions were lightly agitated twice weekly to minimize formation of chemical boundary layers around the membrane.
5. After 5 weeks in solution, the supported membranes were tested for permeability to water, then returned to fresh test solutions.
6. Following an additional 5 weeks in the test solutions (for a total of 10 weeks), the membranes were removed from their solutions and checked again for permeability to water. To minimize any influence of retained solution, the membranes were given the following treatment:
   a. Flush for 30 min with water at 150 psig—to remove residual solution.

   b. Soak in pure water for 5 days—to minimize any residual charge that may have formed on the membrane.
   c. Dry to 60°C overnight, then dry to 250°C for 1 h—to remove any free or adsorbed water. This treatment was observed to return the supported membrane to the same condition that it was when originally tested for permeability.
7. The supported membranes were then checked for permeability to water. These permeabilities were then compared to the pretest permeabilities recorded after 0, 4, and 8 dippings. The equivalent amount of membrane remaining was then determined by interpolation of the permeability data, as demonstrated in Fig. 8. The membrane loss was then calculated as

$$\text{Membrane loss (\%)} = 100(8 - N')/8$$

where N' is the equivalent number of dips remaining after the test.

B. Unsupported Membranes and Clay Support Material

1. Unsupported membranes (prepared by evaporating sol in a dish, then firing) and clay support material were crushed to roughly 20–100 mesh size for efficient contacting with solution.
2. The crushed materials were then placed in seprate containers with the same types of solutions described in A.2. The concentrations of solids in the solutions were approximately 200 ppm (w/w).
3. Same as A.3 and A.4, except that the pH of the solutions was not adjusted.
4. After 10 weeks of testing, the free solution was decanted from any remaining solids, and the decanted solutions tested for dissolved metals.
5. The membrane and clay losses were then calculated as

$$\text{Membrane loss (\%)} = 100 - 100(C_0 - C_f)/C_0$$

where C_0 is the concentration of the metal salt which would be observed if the metal oxide completely dissolves, and C_f is the metal salt concentration which is actually observed at the time in question.

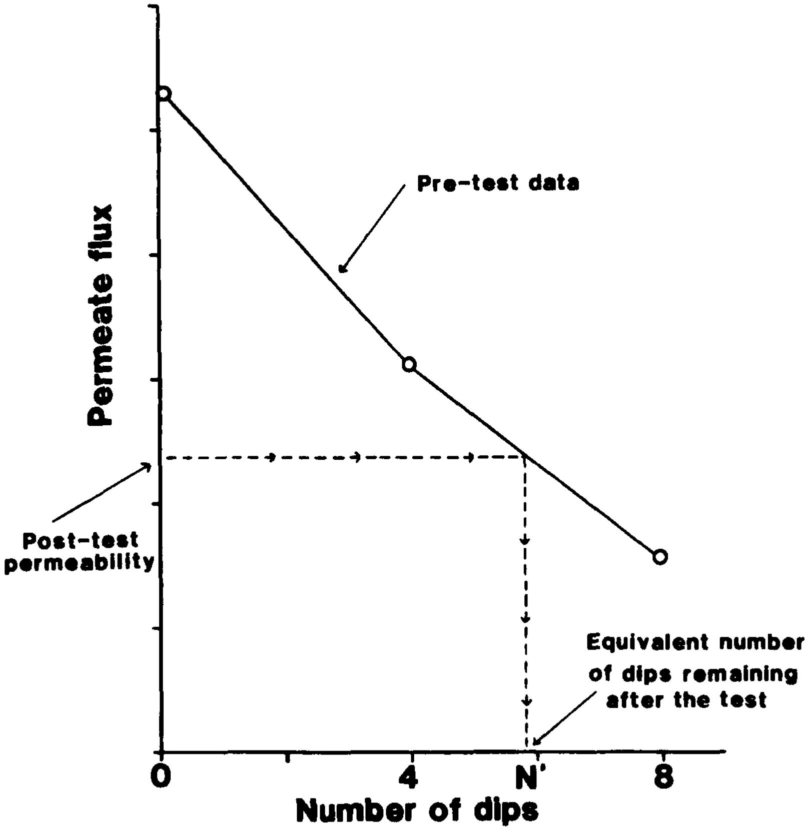

FIG. 8. Method of membrane loss determination for supported membranes (example).

Figures 9 and 10 show the effect of the solution pH on the amount of membrane lost. In the case of alumina, the supported membrane data suggest that minimum loss of membrane occurs at a pH of about 5, while the unsupported membrane suffered virtually no dissolution over the range of pH from 4.4 to 8.3. The shape of the unsupported membrane curve is similar to that of solubility curves given for alumina systems (*10*). However, the solubility did not appear to be a limiting factor. For titania, the supported membrane results were randomly scattered around an average of about 10% loss. The unsupported membrane data showed no loss of titania at any pH.

The clay support material was also very stable. The largest measured

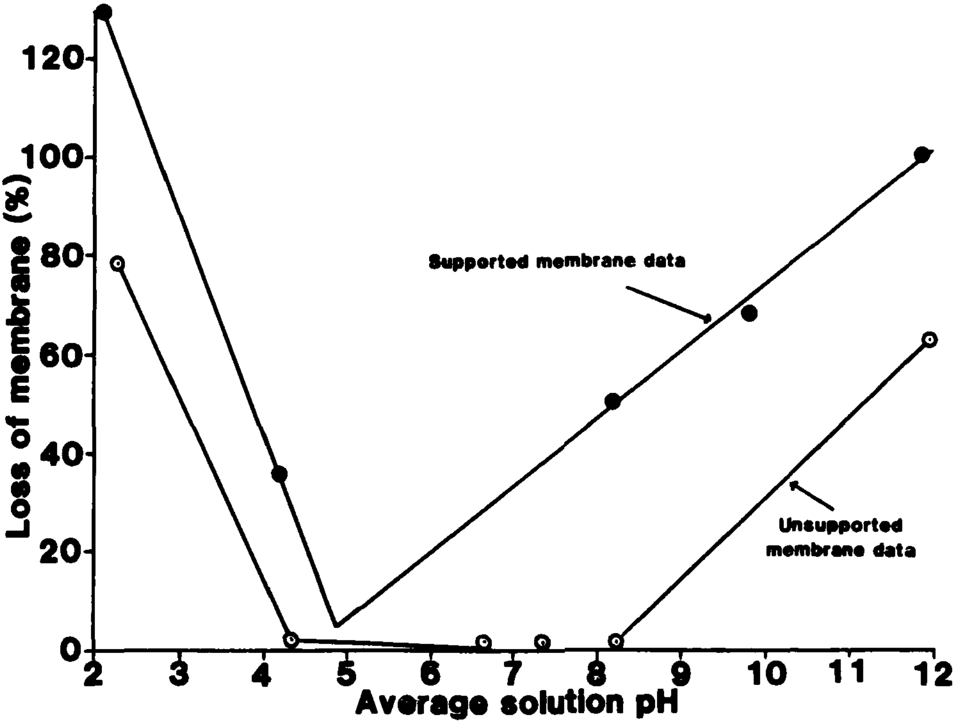

FIG. 9. Loss of alumina membrane in 10 weeks.

loss was 4.8% of the alumina at pH 11.9. All other analyses for aluminum, titanium, and iron indicated losses no greater than 1.1%.

The large difference between the supported and unsupported alumina membrane data suggests that the clay support may have somehow destabilized the membrane. Three additional data points were obtained at pH values of 3, 6, and 9, in this case for alumina membranes on alumina supports. The results were essentially the same as for the alumina-on-clay systems. Thus, from these brief experiments the type of support employed did not appear to affect the stability of the supported membranes.

SUMMARY

Solvent permeability measurements were conducted to ascertain some of the physicochemical properties of ceramic membranes. Permeability

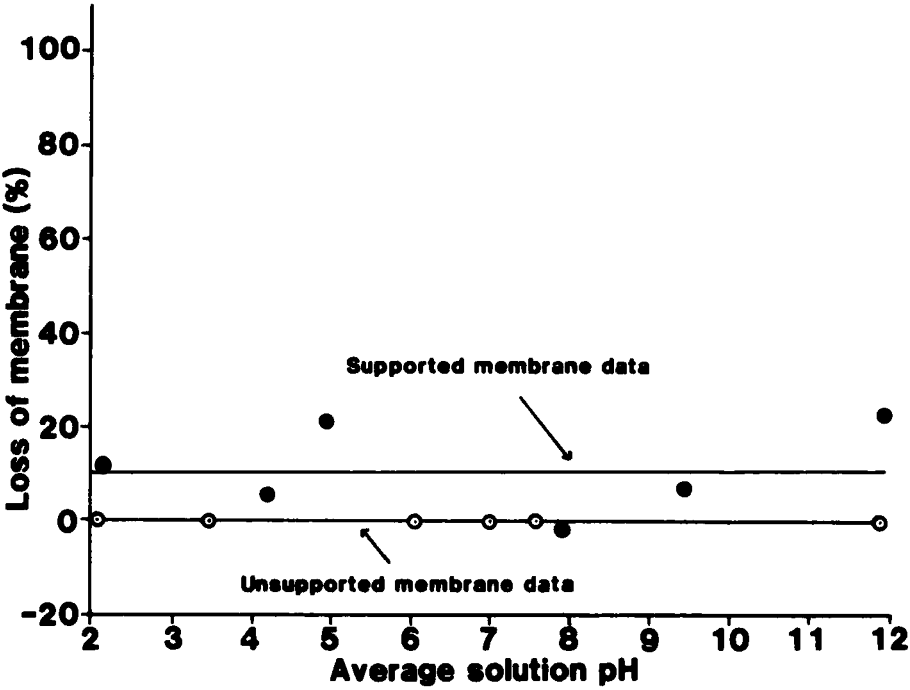

FIG. 10. Loss of titania membrane in 10 weeks.

to water was found to have an Arrhenius-like dependence on the feed temperature. Permeability to water declined over a period of time, but this loss could be reversed by drying the membranes in air. Permeability was affected by the pH of the feed, with maximum flux occurring near the isoelectric point of the membrane. The stability of the membranes to harsh chemical environments was measured. TiO_2 membranes demonstrated virtually no dissolution in 10 weeks when kept in solutions of pH 2-12, while most of the γ-Al_2O_3 membranes dissolved at pH values of under 4 and above 10. An alternative "wet-dipping" procedure for preparing supported ceramic membranes was found to minimize the effect of dipping time on the amount of membrane deposited on a support.

Acknowledgment

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SYMBOLS

C_f	concentration of dissolved metals at the end of the stability test (ppm (w/w))
C_0	concentration of metal solids at the beginning of the stability test (ppm (w/w))
E	activation energy for solvent permeation (cal/g · mol)
J	pure solvent permeation rate ($cm^3/cm^2 \cdot min$)
J_0	pure solvent permeability coefficient ($cm^3/cm^2 \cdot min$)
N'	equivalent amount of supported membrane remaining at the end of the stability test (dips)
R	gas constant (cal/g · mol · °K)
T	absolute temperature (°K)

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