

# **SYNTHESIS AND CHARACTERIZATION OF ALUMINA MEMBRANE BY SOL-GEL TECHNIQUE**

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## **INTRODUCTION**

Membrane separation technology has successfully been applied for water desalination, solutes recovery, waste streams processing, and recently gas separation. Majority of the commercial membranes available today are organic based polymer membranes, which are generally suitable at temperatures below 100°C, in a narrow pH range, and in the absence of organic solvent. Therefore, they would not be suitable for many industrial processes. Inorganic membranes, since their introduction in early 1970s, are making rapid inroads in many areas such as food and beverage processing, biotechnology application, and water treatment, and in the emerging areas of high-temperature gas separation and catalytic reactors. Inorganic (ceramic) membranes offer many advantages : high temperature stability, mechanical stability under large pressure gradients, resistance to aggressive chemicals, insensitivity to microbiological action, high throughput volume, good control of pore size, and longer lifetime. However, they do suffer from a few limitations at the present state of technology development [1, 2].

Inorganic (ceramic) membranes can be prepared by powder pressing and sintering, particle dispersion, and sol-gel technique. The first two methods lead to symmetric membranes with macropores and are suitable for microfiltration. Supported membrane synthesis by sol-gel technique leads to composite asymmetric membranes and proper processing conditions can produce microporous membranes suitable for ultrafiltration. Sol-gel process involves the hydrolysis of a metal alkoxide (like alumina) in a suitable solution which in turn goes through an irreversible sol-gel transition.

The resulting gel is then dried and heated to rigid oxide material. Sol-gel technique is advantageous because a ceramic is obtained at a relatively low sintering temperature, particle size which controls the pore diameter is small and homogenous, and the cut-off range is very narrow [3, 4]. It appears to be very difficult to prepare crack-free membrane layer and there is practically no published information available on how to get defect-free membranes [2].

The objectives of this preliminary research work were to determine the optimum conditions for sol preparation and to produce supported and unsupported alumina membranes. The membranes were characterized for their pore size and morphology by SEM. Permeability studies have not yet been carried out. Fabrication of a suitable permeator cell is under active consideration.

## MATERIAL AND METHODS

### Sol-Gel Preparation:

Boehmite ( $\gamma$ - $\text{Al}(\text{OH})_3$ ) sol was prepared by boiling a mixture of aluminium trihydroxide for - 3 hours and cooling it down to room temperature.  $\text{HNO}_3$  was used as peptizer and polyvinylalcohol (PVA) with a MW of 50,000 was used as organic binder. Many combinations were tried based on literature [2, 4]. However, the following combination gave the best result [5]:

23.4g of  $\text{Al}(\text{OH})_3$  in 400 ml of distilled water boiled for 3 hours gives 18g boehmite in solution. The Boehmite solution (18g boehmite, 34.5g water) was peptized by the addition of 1.5g of 2M  $\text{HNO}_3$ . The solution was boiled under reflux and continuous stirring between 90 - 100°C for a minimum of 6 hours (solution A). A 12% PVA solution (33% by wt) with 12.5%  $\text{HNO}_3$  was prepared in hot water and cooled (solution B). After the peptization process solutions A and B were mixed and stirred for half an hour to obtain a homogenous sol solution, and stored for sol aging.

### Membrane Preparation :

The supporting material were porous ceramic sheet having a thickness of 3mm and flat alumina membrane sheet 0.5mm thick, produced by pressing process. The average pore size for both of these supports was 1.2  $\mu\text{m}$ .

The supports were dipped into the sol for about one minute forming a layer on the surface and filling the pores. The coated supports were dried at 40°C for 48 hours. They were then fired at 500°C for 2 hours and then held at 500 - 1500°C for 3 - 4 hours according to a programme. The sintered membranes were cooled gradually to avoid cracking.

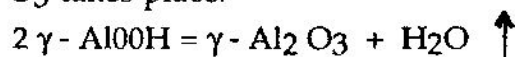
### Analytical Methods:

Production of boehmite powder from aluminium hydroxide was ascertained by density measurement using multipycnometer. Morphology and pore size of the membranes produced were studied by scanning electron microscope SEM.

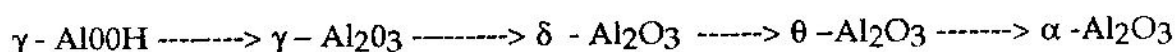
## RESULTS AND DISCUSSION

Boehmite gel was obtained for solutions of  $\text{pH} < 1.1$  confirming the previous work [6]. The optimum acid concentration that resulted in a clear gel was 0.09 mol/mol alkoxide. Supported gel layers were formed by dipping into a gel for a minute or so (slip-casting process). Formation of gel layer and the casting rate depends on a large number of parameters in a complex way. The observations were similar to one reported earlier [2]. The gel layer thickness increases linearly with the square root of dipping time indicating that a slip-casting process is operative. One minute time for dipping was found appropriate. Aging of the sol profoundly affects the casting and also on the pore size (varied from 14 - 162 hours).

The xerogel (membrane layer) obtained after drying was calcined (sintered) over a wide range of temperature 500 - 1500°C. At 390°C the transition of boehmite to  $\gamma\text{-Al}_2\text{O}_3$  takes place:



With increasing temperature and time, the mean pore diameter increases gradually. At  $T > 1000^{\circ}\text{C}$ , very stable  $\alpha$  - alumina phase appears\*. The transformation sequence is [6]:



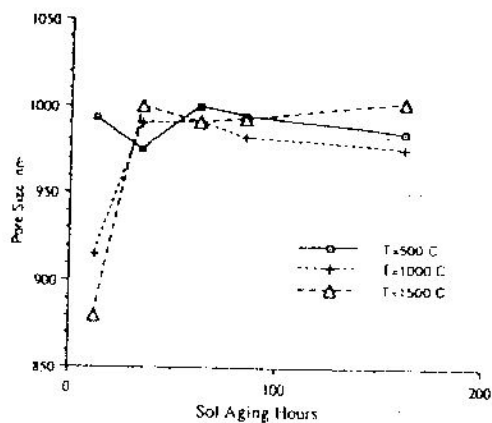
Effect of sol-aging time and calcination temperature one shown in Figures 1 and 2 respectively. It appears that a minimum sol-aging time of 36 hours is necessary. Increase in calcination temperature above  $1000^{\circ}\text{C}$  appears to have slight effect on pore size. A typical example of pore size distribution for a sample prepared at a sol-aging time of 36 hours is shown in Figure 3. Figure 4 shows the surface of a membrane support prepared by pressing process, while Figure 5 gives a micrograph of a sol-gel membrane. Surface of an unsupported membrane is shown in Figure 6.

## CONCLUSIONS

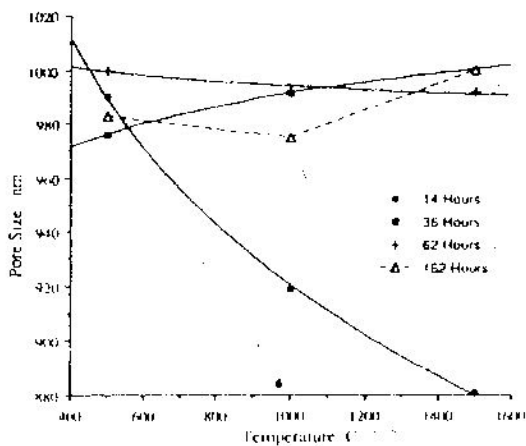
It was concluded that supported alumina membranes by sol-gel process could be prepared. Effect of acid concentration, sol concentration, and binder was established. Crack-free membranes can be prepared by proper selection of binder and plasticizer. A sol aging time of more than 36 hours and calcination temperature of above  $1000^{\circ}\text{C}$  gave membranes with pore size around  $1\text{ }\mu\text{m}$  suitable for microfiltration. Suitable selection of support and casting procedure would improve pore size. The results of this preliminary research are quite encouraging and future work in the direction of selection of suitable support, narrowing pore size and permeability studies is envisaged.

## REFERENCES

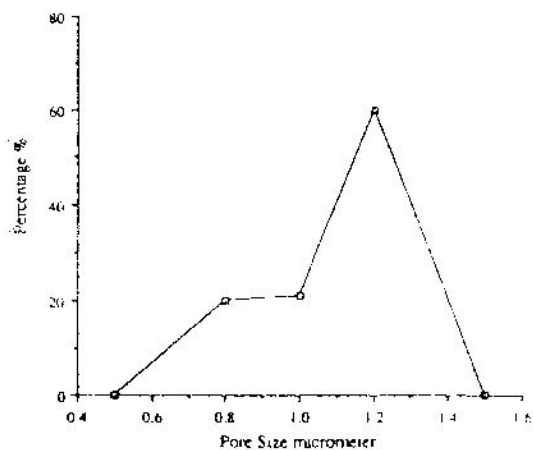
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3. Yoldas, Ceramic Bulletin, **54** (3), 289-290 (1975).
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5. Larbot, et al., New Inorganic UF Membranes, Int. J. of High Tech. Ceramics, Applied Science, 143-151 (1987).
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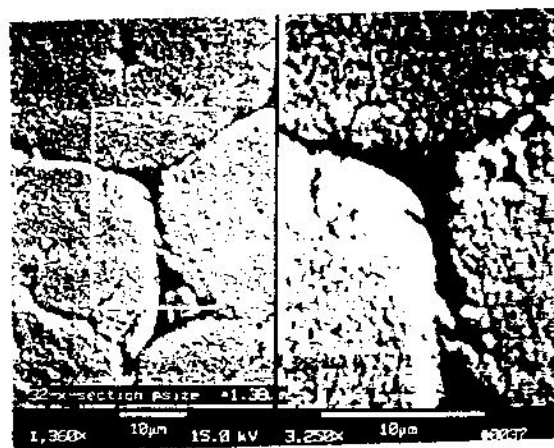
**Figure 1 : Development Of Membrane Pore Size With Sol-Aging Time**



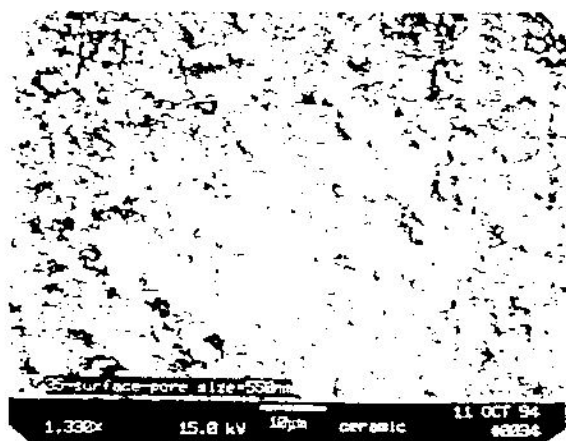
**Figure 2 : Pore Size Development As A Function Of Calcination Temperature**



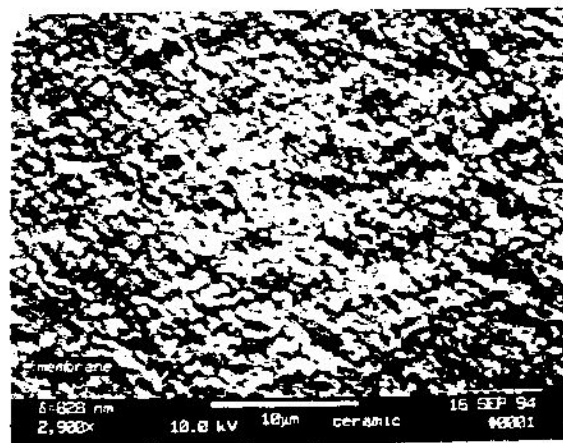
**FIGURE 3 : Pore Size Distribution Of Alumina Membrane Sol-Aging Time, 36 hrs, T=1500 C**



**Figure 4 : Alumina Membrane Membrane Sheet Support**



**Figure 5 : Micrographic Surface of Membrane Calcined At 1000 C**



**Figure 6 : Micrographic Surface Of Unsupported Membrane**