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CHARACTERISTICS OF CERAMIC MEMBRANES DERIVED FROM METAL-OXIDE NANOPARTICLES

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

MASTER OF SCIENCE

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Houston, Texas

January, 2001
ABSTRACT

Carboxylate alumoxanes were cast onto alpha-alumina supports by slip-coating to develop asymmetric ceramic membranes. Carboxylate ferrooxanes were also analyzed as possible precursor for ceramic membranes. Different support materials were studied. Membrane layers as thin as 1 or 2 μm were achieved. The effect of sintering conditions was investigated. The molecular weight cut off was evaluated for these membranes and compared to pore size data obtained by nitrogen adsorption in an effort to correlate pore size and actual performance of the membrane. Membranes were sintered at temperatures between 600°C and 1100°C. The pore sizes increased with higher sintering temperature, from 7 nm at 600 °C to 10 nm at 1000°C, followed by a sharp increase due to the transformation to alpha alumina at higher firing temperatures. The molecular weight cut off showed no considerable variation up to 1000°C. These results are in good agreement with equations reported by several authors that correlate molecular weight with size.
ACKNOWLEDGMENTS

I must first thank Dr. Mark Wiesner for his guidance and support during this project, and very specially for providing me with the opportunity of being part of Rice University. I especially thank Dr. Joe Hughes for his valuable help in the lab and everybody in Dr. Hughes' group for sharing their lab and their experience with me. I thank Chuan-Yue Wang for being such a great help in everything I asked her. Also, I want to thank the other members of my committee Andrew Barron, Mason Tomson and Jerome Rose for devoting their time and advice, specially Dr. Barron and the members of his group, Chris, Cullen, Kim.

I also thank the past members of my group for so many things I could not possible list here: Diane, Julia, Erin, Shawn, Rik and MaryAnn. I can not forget to thank my current group for their friendship and support during these two years: Vladimir, Sarah and Karen. I want to thank also everybody at the Department for the good times we spent together and for many more to come; Emily and Heather for the great parties outside. I thank Jean-Yves Bottero and C.E.R.E.G.E. for providing me with opportunity of visiting their laboratories at Aix-en-Provence and discuss my research with them. I want to thank specially Jerome Rose for his valuable guidance and insights, and also for his friendship and collaboration along this work.

I must also thank my family for their continuing support (and for the endless phone calls). Finally I need to thank very specially to my husband Franchi for all those innumerable things I could not possible have done without him.
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Chapter 1

Introduction

Significance of Research

Membrane technology has found an increasing number of applications over the past decades. From food, beverage and pharmaceutical industries to environmental processes, such as waste water and drinking water treatment, membranes are proving to be cost effective in replacing traditional purification techniques. The expansion of membrane processes is in part dependent on the development of membranes with improved performance fabricated from new materials. Organic membranes are more widely used in industry today than are inorganic membranes. They are found in a variety of pore sizes and formats, tailored to specific applications. However, organic membranes exhibit a number of limitations compared to inorganic membranes. Their thermal resistance is typically limited to temperatures below 200°C, they are less tolerant to the presence of organic solvents and may be vulnerable to microbial attack. On the other hand, ceramic membranes are suitable for high temperature applications, are resistant to solvents and have high mechanical strength. However, they have not been extensively used in the past due to the difficulty and high cost of manufacturing of ceramic membranes with small pore sizes. In the 1970's, with the development of the sol-gel process ceramic composite membranes could be obtained with smaller pores and in a controlled
manner. A drawback of this technique is that it often involves strong acids and other toxic substances, such as trichloroethylene (TCE) and other solvents. As membranes find more and more applications in the environmental field, the question is naturally raised if it is not possible to produce ceramic membranes in a less energy intensive and less pollutant manner. Alumoxane derived membranes appear to offer an environmentally friendly alternative for the manufacture of ceramic ultrafiltration membranes and at a lower cost than the methods currently utilized in the ceramic industry. The availability of membranes with satisfactory properties for a broad range of application at competitive costs will determine the future rate of growth of membrane processes.

**Objectives of Research**

Previous research in our group has determined the potential of alumoxane particles as precursors for ceramic ultrafiltration membranes. The purpose of the present work is:

1. Identify a ceramic support on which alumoxane particles could be cast to form asymmetric membranes, by similar techniques as used in the sol-gel process.

2. Characterize the separation properties of the alumoxane derived ultrafiltration membranes.


4. Determine if ferrooxanes are viable precursors to ultrafiltration membranes and perform a preliminary characterization.
Chapter 2

Literature Review

*Membranes*

A membrane is a permselective barrier or interface between two phases (Figure 1).

![Diagram of membrane process]

Figure 1. Schematic representation of membrane processes.
Separation occurs because the membrane is capable of transporting one component from the feed mixture while retaining others. This selective transport occurs in response to a driving force such as a gradient in concentration, pressure, temperature, or electrical potential.

Membranes can be classified as natural, or biological as for example in bacteria, and synthetic. Synthetic membranes can be further divided between organic (polymeric or liquid) and inorganic (ceramic, metal) membranes.

According to their structural characteristics, two categories can be recognized: dense and porous membranes. Dense membranes are free of discrete, well defined pores or voids.

The microstructure of a porous membrane can vary, as shown in figure 2.

![Diagram of straight-pore and tortuous-pore membranes]

Figure 2. Cross sectional schematic diagrams of various types of porous membranes

Those membranes that show essentially straight pores across the membrane thickness are referred to as straight pore membranes. The majority of the porous membranes, however,
have interconnected pores with tortuous paths and are called tortuous pore membranes. Another means of classifying membranes is with respect to their structure. In symmetric membranes, the material has the same properties along its thickness. Asymmetric membranes have a very dense top layer or skin of low thickness supported by a more permeable sublayer. The asymmetric membrane combines high permeability due to a thin skin layer with high selectivity and good mechanical strength provided by the support.

Figure 3. Schematic representation of symmetric and asymmetric membranes cross sections.

Membrane processes can be operated in two different ways with respect to the direction of flow: crossflow and dead-end filtration.

In crossflow filtration, the feed stream flows parallel to the membrane surface, the permeate penetrates through the membrane in the direction normal to the surface.
Figure 4. Cross flow filtration.

In dead-end or frontal filtration, the flows of the feed stream and the permeate are both perpendicular to the membrane surface.

Figure 5. Dead-end filtration

Pressure is the driving force in most of the separation processes currently applied at the industrial scale for water or wastewater treatment. Pressure-driven processes can be further classified by the pressure of operation and a typical flux range, as shown in Table 1.
<table>
<thead>
<tr>
<th>Membrane Process</th>
<th>Pressure Range</th>
<th>Specific Permeate Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>bar</td>
<td>1 / ( m^2 * h * bar )</td>
</tr>
<tr>
<td>microfiltration</td>
<td>0.1 - 2.0</td>
<td>&gt; 50</td>
</tr>
<tr>
<td>ultrafiltration</td>
<td>0.5 - 5.0</td>
<td>10 - 50</td>
</tr>
<tr>
<td>nanofiltration</td>
<td>5.0 - 20</td>
<td>1.4 - 12</td>
</tr>
<tr>
<td>reverse osmosis</td>
<td>10 - 100</td>
<td>.005 - 1.4</td>
</tr>
</tbody>
</table>

Table 1. Pressure driven membrane processes.

The application range of each process is illustrated in Figure 6.

The application range of each process is illustrated in Figure 6.

Particle Size

<table>
<thead>
<tr>
<th>µm</th>
<th>0.001</th>
<th>0.01</th>
<th>0.1</th>
<th>1</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>100</td>
<td>200</td>
<td>1000</td>
<td>100,000</td>
<td>500,000</td>
</tr>
</tbody>
</table>

Ag. Salt | Colloidal Silica | Yeast Cells
Virus | Bacteria

Solutes

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Proteins</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar</td>
<td>Microsolutes</td>
</tr>
</tbody>
</table>

Membrane Process

Figure 6. Application range for membrane processes.
History & Development

While conducting an experiment to study the ebullition of liquids, Jean Antoine Nollet in 1748 noted that water passed through a wet pig bladder while rejecting almost entirely the passage of ethanol. He could not explain the phenomenon at the time. In the first half of the nineteenth century, Thomas Graham performed an extensive experimental investigation on dialysis and diffusion of salts in water. In response of Graham's work, Adolph Fick proposed in 1855 the fundamental law of diffusion. Fick drew a parallel to the diffusion of heat (Fourier's law) and that of electricity (Ohm's law) to model the diffusion of molecules in a solvent. A number of theoretical considerations were studied in the first part of the twentieth century: Donnan investigated ionic effects in separation as part of a study of soaps in solution. In the field of physiology, Meyer and Strauss (1940) conducted research on electrodialysis. Kedem and Katchalsky (1964) applied irreversible thermodynamics to describe transport processes through membranes, where free energy is dissipated continuously. Other transport models followed: Lonsdale (1965) proposed the solution-diffusion model to explain the transport of a gas, vapor or liquid through a dense, non-porous membrane.

The first commercial membrane was produced by Sartorius in Germany, after World War I. These membranes were used only on a laboratory scale, mostly applied to bacteria filtration. A breakthrough in membrane technology occurs in 1965 with the development of the asymmetric membrane, with much higher permeation rates due to the very low thickness of the permeation barrier.

Membrane processes are used today in a wide variety of environmental applications, from fuel cells to air pollution control, resource recovery and water treatment.

The membrane technologies market has risen from $363 millions in 1987 to more than $1 billion in 1997. Approximately 40% of membrane sales is destined for water and waste water treatment applications. Food and beverage processing combined with pharmaceuticals and medical applications account for another 40% of sales. The use of membranes in chemical
and industrial gas production is growing. This broad range of applications and a projected sales growth to $1.5 billion by 2002 suggests that membrane technologies are now well accepted and cost effective, conferring unique advantages over previous separation processes. Improvements in the underlying technology, a more competitive market, a more demanding regulatory environment, a broader range of membrane processes, and the availability of new materials from which membranes can be fabricated are driving the expansion in environmental applications.

Ceramic Membranes

Microporous membranes made of porcelain were studied in the beginning of this century, and in the 1940’s glass membranes became popular for micro-filtration applications.

The first large scale application of porous ceramic membranes arose from the World War II Manhattan Project in the 1940’s. They were used as gaseous diffusion barriers in the Uranium enrichment process.

In the 1970’s, the same technology of uranium isotope separation was applied to liquid micro and ultrafiltration in France.

At present, a variety of ceramic membranes are available for industrial applications, such as food and beverages processes, waste water and water / oil treatments and biotechnology separations.

Inorganic membranes have several properties that make them more suitable for certain applications than organic membranes. Ceramic membranes are more tolerant to extreme pH and temperature (Table 2). While the majority of organic membranes begin to deteriorate around 100°C, inorganic membranes can be used at temperatures well above 500°C. Inorganic membranes can withstand organic solvents, chlorine and other chemicals better than organic
membranes. Ceramic membranes are not susceptible to microbial attack and do not suffer from problems of mechanical stability and compaction during operation at high pressure.

Although inorganic membranes present unique advantages over organic membranes, their development have been relatively slow in comparison to the latter. Organic membranes are much more wide-spread used today. This is, in part, a consequence of the cost and difficulty in producing crack-free ceramic membranes with narrow pore size distributions.

In spite of that, the world market for inorganic membranes, excluding uranium separation, grew from $12 million in 1986 to $35 million in 1990.

<table>
<thead>
<tr>
<th>Material</th>
<th>Applications</th>
<th>Maximum working temperature (°C)</th>
<th>pH range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acetate</td>
<td>RO, UF, MF</td>
<td>50</td>
<td>3 - 7</td>
</tr>
<tr>
<td>Aromatic polyamides</td>
<td>RO, UF</td>
<td>60 - 80</td>
<td>3 - 11</td>
</tr>
<tr>
<td>Fluorocarbon</td>
<td>RO, UF, MF</td>
<td>130 - 150</td>
<td>1 - 14</td>
</tr>
<tr>
<td>Polyimides</td>
<td>RO, UF</td>
<td>40</td>
<td>2 - 8</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>UF, MF</td>
<td>80 - 100</td>
<td>1 - 13</td>
</tr>
<tr>
<td>Nylons</td>
<td>UF, MF</td>
<td>150 - 180</td>
<td></td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>UF, MF</td>
<td>60 - 70</td>
<td></td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td></td>
<td>120 - 140</td>
<td></td>
</tr>
<tr>
<td>PVDF</td>
<td>UF</td>
<td>130 - 150</td>
<td>1 - 13</td>
</tr>
<tr>
<td>Polaphosphazene</td>
<td></td>
<td>175 - 200</td>
<td></td>
</tr>
<tr>
<td>Alumina (gamma)</td>
<td>UF</td>
<td>300</td>
<td>5 - 8</td>
</tr>
<tr>
<td>Alumina (alpha)</td>
<td>MF</td>
<td>&gt; 900</td>
<td>0 - 14</td>
</tr>
<tr>
<td>Glass</td>
<td>RO, UF</td>
<td>700</td>
<td>1 - 9</td>
</tr>
<tr>
<td>Material</td>
<td>Process</td>
<td>Temperature</td>
<td>pH</td>
</tr>
<tr>
<td>------------------------------</td>
<td>---------</td>
<td>-------------</td>
<td>----</td>
</tr>
<tr>
<td>Zirconia</td>
<td>UF, MF</td>
<td>400</td>
<td>1-14</td>
</tr>
<tr>
<td>Zirconia (hydrous)</td>
<td>RO, UF</td>
<td>80 - 90</td>
<td>4-11</td>
</tr>
<tr>
<td>Silver</td>
<td>MF</td>
<td>370</td>
<td>1-14</td>
</tr>
<tr>
<td>Stainless steel (316)</td>
<td>MF</td>
<td>&gt;400</td>
<td>4-11</td>
</tr>
</tbody>
</table>

Table 2. Characteristics of inorganic and organic membranes. (Hsieh, 1996).

Membrane Characterization

Membrane characterization provides information necessary to monitor membrane production, predict performance, and make comparisons between membranes. In the case of a new material, characterization is a key component in identifying applications and markets to which new membranes might be introduced.

X-ray powder diffraction

X-ray powder diffraction is used to obtain information about the structure, composition and state of polycrystalline materials. The equipment consists of a high voltage source, an X-ray tube, a goniometer and a detector (Figure 7).
The tube contains a tungsten filament and a metal anode. When an electric current passes through the filament, electrons are emitted and accelerated by the applied voltage. The electrons hit the anode and produce X-rays. The emission of X-rays takes a very low portion of the energy produced, more than 99% is converted to heat and must be eliminated by refrigeration by water. The tube is under vacuum (10^-6 mm Hg) and has Beryllium windows through which the X-rays exit. The analysis of minerals requires a monochromatic X-radiation; this is achieved by a filter or a monochromator at the exit of the tube.

When a beam of monochromatic X-radiation is directed at a crystalline material reflection or diffraction of the X-rays is observed at various angles with respect to the incident beam. The relationship between the wavelength of the X-ray beam, \( \lambda \), the angle of diffraction, \( 2\theta \) and the distance between each set of atomic planes of the crystal lattice, \( d \), is given by the Bragg condition:

\[
n * \lambda = 2 * d * \sin \theta
\]  
(1)
where \( n \) represents the order of diffraction. From this equation we can calculate the interplanar distances of a crystalline material.

The X-ray pattern of the crystalline substance can be though of as a "fingerprint"; each crystalline material has a unique diffraction pattern. The Joint Committee on Powder Diffraction Standards (JCPDS) has published the powder diffraction patterns of some 50,000 compounds. An unknown compound can be identified by comparing its pattern with those in the powder diffraction file.

**Surface Topography**

**AFM**

The concept of Atomic Force Microscopy (AFM) scanning was first presented by Binning and Quate in 1986. Images are obtained by measurement of the force on a sharp tip placed in proximity with the surface of the sample. In Tapping Mode AFM, a vibrating tip is brought into intermittent contact with the surface. When the tip interacts with a surface feature, its amplitude is decreased from the previous amplitude of oscillation. The AFM senses this decrease and the tip is raised away from the surface until it regains its original amplitude. In this way, the tip will follow the contours of the surface as it moves along the sample.

Pradanos et al. (1996) found AFM a useful technique to characterize the surface structure of a membrane, especially because it allows for the analysis of dry and wet samples without any prior treatment. However, Pradanos noted that AFM overestimates pore sizes depending on the pore entrance size and the shape and size of the tip. One reason for this is that the AFM can only measure the maximum diameter of the pore at the membrane surface and the pores are supposed to be funnel-shaped; on the other hand, SEM tends to underestimate pore
diameters by at least 1 nm due to the metal coating (Dietz et al., 1992). Several researchers (Calvo et al. (1997), Bowen et al. (1996)) recognize the problem of the convolution between the tip shape and the pore, when the tip touches the surface at two positions at the same time. Bowen et al. (1996) examined Anopore membranes with both contact and non-contact AFM and determined pore sizes distributions based on their scanned images. Zeng et al. (1997) performed a surface morphology study of ceramic membranes by AFM; they studied the roughness of the surfaces but pore sizes could not be determined due to the bumpy characteristic of the samples.

**SEM**

Scanning electron microscopy is another tool that can be used to study surface topography of solid materials. The resolution of the scanning electron microscope is about 3 nm.

Figure 8 represents a schematic of a scanning electron microscope.
Figure 8. Scanning Electron Microscope.

A narrow beam of high energy electrons, primary electrons, is focused on the sample. Secondary electrons are not reflected, but rather are liberated from atoms in the surface, and they determine the image.

Some sample preparation is required. The sample needs to be coated with a conductive layer, often a gold layer, to prevent charging up of the surface, which may result in damage or burning of the sample.

SEM can be used to view the surface structure of membranes, evaluate cross sections, identify asymmetric filters and obtain measurements of pore size, pore size distribution and surface porosity.
Pore size and pore size distribution

The membrane pore size is important not only in determining membrane permeability but also in determining membrane selectivity; which solute will pass or will be retained. Models for flow through porous media typically make simplifications regarding the geometry of the pore. For example, in the Poiseuille equation the pores are considered to be parallel cylinders, while in the Carman Kozeny equation the pores are regarded as part of a system of close-packed spheres of equal diameter. In addition, it is not the pore size which is the rejection determinant factor, but the smallest constriction within the porous body. Some techniques, such as AFM, determine the dimensions of the pore entrance rather then the pore size. In order to interpret the results of a particular characterization technique, it is essential to be aware of all the assumptions and limitations.

In general, the pores in the membrane are not all of the same size, but exist as a distribution. The membrane can then be characterized by a mean pore size and standard deviation. A low standard deviation, indicating a narrow pore size distribution, is desirable because it results in improved separation performance and sharp molecular weight cut off (see section on MWCO). The mean pore size corresponds to the first moment of the distribution; however particles bigger than the mean pore size will pass through the membrane, depending on the width of the distribution. Pore sizes often exhibit a log-normal distribution, with the tail towards bigger pore sizes (Figure 9). Another way to describe the pore size or pore volume distribution of a porous membrane is a cumulative distribution (Figure 10), that indicates the percentage of pore volume corresponding to pores of a determined size and bigger.
Figure 9. Pore size distribution of a porous membrane.

Figure 10. Volume of pores with size less than the stated pore size.
A classification of pores according to their size was proposed by Dubinin (1960) and later officially adopted by the IUPAC (Table 3).

<table>
<thead>
<tr>
<th>Micropores</th>
<th>&lt; 2 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesopores</td>
<td>2 nm - 50 nm</td>
</tr>
<tr>
<td>Macropores</td>
<td>&gt; 50 nm</td>
</tr>
</tbody>
</table>

Table 3. IUPAC classification according to pore diameter

**Nitrogen Adsorption/Desorption:**

The adsorption of a gas by a solid can supply valuable information with respect to the surface area and pore structure of the solid. In practice, the most commonly used adsorbate is nitrogen at its boiling point, 77 K.

The adsorption isotherms can be grouped into five classes, originally proposed by Brunauer, Emmett and Teller (Figure 11).

Type II isotherms indicate that the solid is non-porous while type IV isotherms are characteristic of mesoporous solids. From both types of isotherms it is possible to calculate the surface area of the solid, and for the type IV isotherm pore size distribution may also be determined.

The surface area and pore size distribution of a sample is calculated from all or part of the adsorption and desorption isotherms. The adsorption isotherm is an incremental set of data which describes how much adsorbate gas, nitrogen in our case, condenses on to a material at a given pressure and at a constant temperature. Desorption is the reverse process and is a decremental set of data reported in the same units.
Figure 11. The five types of isotherm Brunauer, Emmett and Teller classification. (Gregg and Sing, 1982)

The BET model

The BET model is based on the Langmuir kinetic model of the adsorption process. Equation (2) is the Langmuir equation for the case of monolayer adsorption.

\[
\frac{n}{n_{\infty}} = \frac{B \cdot p}{1 + B \cdot p} \quad (2)
\]
where

\( n \) is the number of moles, adsorbed on 1 g of adsorbent,

\( n_m \) is the monolayer capacity

\( p \) is the partial pressure of the gas and

\( B \) is an empirical constant.

The surface of the solid is regarded as an array of adsorption sites. The Langmuir model proposes a dynamic equilibrium, in which molecules of the gas condense on open sites at the same rate at which molecules evaporate from occupied sites. This evaporation-condensation mechanism can also be applied to second and higher molecular layers; however the assumptions inherent in the Langmuir isotherm are quite constraining.

Brunauer, Emmett and Teller introduced some simplifying assumptions to the Langmuir model to derive their equation for multilayer adsorption:

1. in all layers except the first the heat of adsorption is equal to the molar heat of condensation;

2. in all layers except the first, the evaporation-condensation conditions are identical and,

3. when the partial pressure of the adsorptive equals its saturation pressure, it condenses to a bulk liquid on the surface of the solid, i.e., that the number of layers becomes infinite.

These three assumptions lead to the BET equation:

\[
\frac{p/p^o}{n*(1 - p/p^o)} = \frac{1}{n_m*c} + \frac{(c-1)*p/p^o}{n_m*c} \tag{3}
\]
where \( c \) is a parameter that depends on the heat of adsorption.

Due to the constrains these assumptions impose, the model has been subject to a number of criticisms. Gregg and Sing (1982) summarize its limitations. The model assumes that all the adsorption sites are energetically identical, i.e. there are no preferential adsorption sites. In fact, surfaces are often heterogeneous. The model focuses on the forces between adsorbent and adsorbate molecules and neglects interactions between molecules of adsorbate in the same layer; however, these "horizontal" interactions become important as a layer approaches completion. It is also questionable if all layers after the first can be treated equally, since interaction energies diminish as distance from the solid surface increases.

**The Kelvin Equation**

Mesoporous solids show type IV isotherms, with its characteristic hysteresis loop. Zsigmondy proposed a model to explain these isotherms. He assumed that the initial part of the isotherm, \( ABC \) in Figure 13, is restricted to a thin layer on the walls, until \( D \), when capillary condensation occurs in the smallest pores. As the pressure is increased, bigger pores are filled, until at saturation pressure the entire system is full of condensate. The model was based on a principle established by Lord Kelvin, that the equilibrium vapor pressure over a concave meniscus of liquid must be less than the saturation vapor pressure at the same temperature due to capillary forces. This implies that a vapor will be able to condense in the pores of a solid, even if its relative pressure is less than one. The relationship is established in the Kelvin equation:
\[
\ln \frac{p}{p^0} = \frac{-2 \gamma V_L}{R T r_m}
\] (4)

where

\(p/p^0\) is the relative pressure of the vapor in equilibrium with the meniscus having a radius of curvature \(r_m\),

\(\gamma\) is the surface tension of the liquid adsorptive,

\(V_L\) is its molar volume,

\(R\) is the gas constant and

\(T\) is the temperature.

Figure 12. \(r_m\) of the Kelvin equation for a cylindrical pore and zero angle of contact.

If the pores are assumed to be cylindrical and the angle of contact to be zero, the meniscus is spherical and the mean radius of curvature from the Kelvin equation becomes equal to the radius of the pore, minus the thickness of the already adsorbed film on the walls (Figure 12).

From point D in the isotherm and using the Kelvin equation, it is possible to calculate the minimum radius of pore in which capillary condensation can occur. It varies from system to
system, but it is rarely below 1 nm and it becomes the lower detection limit for the method. The upper limit is set by the experimental difficulties of measuring very small differences in vapor pressure.

![Graph showing a type IV isotherm](image)

**Figure 13.** A type IV isotherm (from Gregg & Sing, 1982)

**Permeability**

The permeability of the membrane is a measurement of its ability to allow fluid to pass through it in response to a pressure gradient. The higher the permeability, the higher the permeate flux, and less membrane area is required to supply a given design flow.
The permeability is inversely proportional to the resistance of the membrane, \( R_m \).

Membrane resistance, the pressure applied across the membrane, \( \Delta P \), and the resulting permeate flux are related to one another by Darcy’s law expression of the form:

\[
J = \frac{\Delta P}{\mu \times R_m}
\]  

(5)

where

\( J \) is the permeate flux, \( \text{[volume / (area \times time)]} \),

\( \Delta P \) is the transmembrane pressure,

\( \mu \) is the viscosity of the solution being filtered, water in this case, and

\( R_m \) is the resistance of the membrane.

If it is assumed that flow in the pores of the membrane can be described by Poiseuille’s law, then the flow across the membrane in a single pore can be described as:

\[
J_p = \frac{r_p^2 \times \Delta P}{8 \times \mu \times \tau \times l}
\]  

(6)

where

\( r_p \) is the radius of the tube,

\( l \) is its length, and

\( \tau \) represents the tortuosity factor, which relates the actual path of the permeate through the membrane to its thickness. The total flux through the membrane, \( J \), is obtained multiplying \( J_p \) times the surface porosity, \( \varepsilon \).
\[ J = \varepsilon \cdot J_p = \frac{\varepsilon \cdot r_p^2 \cdot \Delta P}{8 \cdot \mu \cdot \tau \cdot l} \]  

(7)

Comparing this expression to Darcy’s law, it follows that

\[ Rm = \frac{\varepsilon \cdot r_p^2}{8 \cdot \mu \cdot \tau} \]  

(8)

Darcy’s law can also be expressed in terms of permeability, \( k \).

\[ J = \frac{k \cdot \Delta P}{\mu \cdot l} \]  

(9)

and

\[ k = \frac{\varepsilon \cdot r_p^2}{8 \cdot \tau} \]  

(10)

Equation (10) can be applied to calculate the membrane permeability. If the tortuosity factor is assumed to be 1, Poiseuille’s flow (straight pores), the maximum theoretical flux is obtained. Transmembrane pressure, viscosity, pore size and thickness can be measured by other techniques.
Molecular Weight Cut Off

The molecular weight cut off (MWCO) is a specification that describes the retention capabilities of a membrane. It is defined as the molecular weight of a solute which is 90% rejected by the membrane. It can also be regarded as an indication of the pore size of the filter. A sharp cut off, or a very steep MWCO curve, is an indication of a narrow pore size distribution, while a diffuse cut off is a sign of a wider distribution in pore sizes. (Figure 14)

![Retention curves for two different membranes, sharp and diffuse cut off.](image)

The ASTM sets a standard for the determination of the MWCO of flat ultrafiltration membranes with cut offs between 4,500 and 1,000,000 daltons. The test solution, a mixture of dextran fractions that covers the above molecular weight range, is filtered. Both the feed and the permeate are characterized by Gel Permeation Chromatography to determine molecular weight distribution of solute, and the rejection can be calculated as a function of molecular weight.
The fractional rejection $R_i$, is defined as:

$$R_i = 1 - \frac{c_{i,p}}{c_{i,f}}$$

(11)

where

$R_i$ is the rejection of molecules with a molecular weight of $i$,

$c_{i,p}$ is the concentration of molecules with molecular weight $i$ in the permeate, and

$c_{i,f}$ is the concentration of molecules with molecular weight $i$ in the feed.

Each $R_i$ value can be calculated from the molecular weight distribution curves obtained with Gel Permeation Chromatography (GPC). The value of $R_{90\%}$ is the MWCO for the membrane tested.

In addition to molecular weight, the value of the MWCO obtained is also a function of the shape and flexibility of the test molecule, its interaction with the membrane surface and experimental conditions that can result in concentration polarization and/or fouling. Concentration polarization is the accumulation of the solutes rejected by the membrane near its surface. It negatively affects the purity of the permeate and produces a decline in permeate flux. One cause of fouling is the adsorption of the rejected component on the membrane surface leading to a blockage of pores and potentially a change in rejection characteristics. MWCO determinations should therefore be performed using low feed concentrations, low pressure and high feed velocity to minimize concentration polarization. Transmembrane pressure, cross flow velocity, geometry of the experimental set-up (cross-flow or dead-end filtration), and type of test solute chosen also influence the results. If the same membrane is tested with three types of solute, for example albumin (a globular protein), dextran (a branched polysaccharide) and poly-ethylene glycol (a linear flexible molecule), three different retention values are obtained.
To avoid these effects, different molecule types should not be used and a low tendency to adsorb to the membrane material is also desirable.

Two effects were found to have a fundamental gravity on the transfer of macromolecules (Balmann and Nobrega, 1989). The permeate flux and overall rejection coefficient were found to dependent on operating conditions. Also, the molecular weight distribution of the permeate was affected. These phenomena were attributed to concentration polarization. In their study of the transfer of dextran solutions through a polysulfone hollow fiber membrane, Balmann and Nobrega (1989) showed that when the concentration was increased, a molecular coil of a determined molecular weight occupied a smaller volume and as a consequence, molecules of higher molecular weight could pass through pores that would otherwise retain them. The second mechanism observed was the deformation of the molecules due to the shear stress within the pores of the membrane. In summary, when the permeate flux increases, the apparent size of the polymer chains decreases, while a decreasing concentration at the membrane-solution interface or boundary layer tends to make their apparent size bigger. Thus, the conditions for performing this test must be carefully chosen to avoid the effects of concentration polarization and high permeate flow rates. Hazlett et al. proposed guidelines for characterization of ultrafiltration membranes: the test solute concentration should be between 200 and 1000 ppm to obtain reliable results and at the same time avoid concentration polarization effects; they recommended a permeate flux not exceeding 0.1 % of the recirculation flow through the set up. Dextrans were selected as preferred test molecules to performed molecular weight cut off tests due to their stability with respect to temperature and pH. Several researchers (Balmann et al., Nobrega et al., Meireles et al., Hazlett et al.) pointed out the necessity of the addition of a bactericide, sodium azide, to prevent bacterial growth in the test solution. Ionic strength was set to 0.5 M in most of the cases to screen electrostatic interactions between macromolecules and the different surfaces.
Polymers

Polymers are used in the MWCO determinations as the test molecule. The linear polymer, the simplest kind, is a repeating sequence of a number "n" of monomers A, joined head-to-tail, designated Aₙ. Many homopolymers are formed using a chain initiator, and a chain terminator; for small polymers, the contribution of these two monomers can be important, but becomes negligible as the number of center monomers involved increases. Polymers may polymerized in other ways than the head-to-tail fashion, in which case branched polymers are formed; when the end units are joined, the polymer is known as cyclic.

The dissolution of a polymer has been described as a two steps process; solid swelling and separation and disentangling of the chains. Small molecules have a limited number of ways to interact with itself or other neighboring molecules, but polymers are capable of a variety of interactions. Although these interactions are individually weak, their cumulative effect is responsible for the particular structural properties that polymers show. These are secondary, tertiary and quaternary conformational effects, and they are classified with respect to the increasing distances of the interaction required to maintain intra- or intermolecular associations. They are observed in both biological and synthetic polymers. Secondary structures refer to the main chain bond angles, when the polymer is at equilibrium in solution; the distance along the chain is small for this interaction. The formation of tertiary structures is often a consequence of the interaction of elements of secondary structure. Quaternary structure is a special case of aggregation between distinct chains. The types of interactions that account for the structure of a polymer are relatively few: hydrogen bonding, solvophobicity, ionic interactions and some other special interactions between certain groups, as for example disulfide bonds and aromatic rings. These interactions originate as a result of the competition among solute-solvent, solute-solute and solvent-solvent interactions. Therefore, defining a structure for a given polymer means that the solvent (pH, ionic strength) and the temperature are also defined. Under different conditions, the equilibrium structure will vary.
The molecular parameters used to characterize polymers are molecular weight, molar volume, radius of gyration, hydrodynamic radius, end-to-end distance of the chain, length of principal axes, etc. Higher order moments of the molecular weight average are used to characterize the shape of the distribution of synthetic polymers.

Figure 15 shows a random coil in solution, where $r$ is the end-to-end distance.

![Schematic of a coil in solution](image)

Figure 15. Schematic of a coil in solution.

As the molecular weight of the chain increases (more monomers are added), the dimensions of the coil are often observed to increase with the square root of the molecular weight. The end-to-end distance is related to the radius of gyration by the following expression:

$$r^2 = 6 \times r_g^2$$  \hspace{1cm} (12)
The dimensions of the coil are also often expressed by the hydraulic radius or the Stokes-Einstein radius. For many polymeric solutions, there is an empirical relation between the bulk diffusion coefficient $D_b$ and the molecular weight $M_w$.

$$D_b = a \cdot M_w^{-b}$$  \hspace{1cm} (13)

where $a$ and $b$ are constants characteristic for a polymer and a solvent. The Stokes-Einstein radius can then be calculated by the following equation:

$$r_h = \frac{k \cdot T}{6 \cdot \pi \cdot \eta \cdot D_b}$$  \hspace{1cm} (14)

where

- \( k \) is the Boltzmann constant,
- \( T \) is the absolute temperature, \( (K) \) and
- \( \eta \) is the viscosity.

Several models have been proposed to link the size to the molecular weight. Granath et al. reported the following equation to calculate the radius from the molar mass of dextran:

$$a = 0.33 \cdot (M)^{0.46}$$  \hspace{1cm} (15)

where

- \( a \) is the radius of the dextran molecule in angstroms and
- \( M \) is its molar mass, in grams per mole.
Worch (1993) proposed another correlation, derived from the Stokes Einstein Equation, to relate polymers molecular weight to their size:

\[ r = 2.037 \times 10^{-11} \times (M)^{0.53} \]  

(16)

where

- \( r \) is the radius of the molecule in meters and
- \( M \) is its molar mass, in grams per mole.

**Polymer molecular weight distribution statistics**

The weight-average molecular weight (Mw), number-average (Mn) molecular weight and the polydispersivity ratio (P) can be calculated as:

\[ M_w = \frac{\sum_{i=1}^{n} (h_i \times M_i)}{\sum_{i=1}^{n} (h_i)} \]  

(17)

\[ M_n = \frac{\sum_{i=1}^{n} (h_i)}{\sum_{i=1}^{n} (h_i \times M_i)} \]  

(18)

\[ P = \frac{M_w}{M_n} \]  

(19)
where

$n$ is the number of data slices (chromatographic, PCS),

$h_i$ is the height of the molecular weight distribution curve at the $i$th slice,

$M_i$ is the molecular weight of the species in the $i$th slice, and

$P$ is the polydispersivity. For a monodisperse sample, $M_w$ will be equal to $M_n$, and therefore, $P$ will be one.

There are a number of techniques available to characterize polymers: Gel Permeation Chromatography, sedimentation velocity, viscosimetry, electrophoretic mobility, nuclear magnetic resonance, and light scattering, between others.

**Dextran**

Dextran is a polymer of anhydroglucose. It is composed of approximately 95% $\alpha$-D-$(1\rightarrow6)$ linkages. The remaining $\alpha$-(1→3) linkages account for the branching of dextran (Figure 16).
Figure 16. Dextran macromolecule.

The length of the branches is around three units of glucose, but branches of as much as fifty units have been detected. Lower molecular weight dextrans will exhibit less branching and have a more narrow range of molecular weights. Dextrans with molecular weights greater than 10,000 behave as if they are highly branched. As the molecular weight increases, dextran molecules attain greater symmetry. Between molecular weight of 2,000 and 10,000, they exhibit the properties of an expandable coil, but below 2,000, they are more rod-like.

Within the exemption of the very high molecular weight dextrans in the range of 5 to 40 million grams per mole, dextrans are very soluble in water. They are also soluble in DMSO, formamide, ethylene glycol, and glycerol.

Occurrence in the environment

Polysaccharides are homo- or copolymers of sugar residues joined together. Practically all of the sugar residues are hexoses or pentoses of the aldose type; ketose residues occur rarely in polysaccharides. Glycosidic bonds occur between the sugar residues. The polysaccharide chains may be linear or have comb- or star-shaped branching. Polysaccharides mostly do not occur in the pure state in nature: they most often possess a stable and probably covalent bonded peptide component to the extent of a few percent. This peptide component is rich in hydroxyl groups containing amino acids.

Polysaccharides are found in plants and animals. In higher plants and algae, they are components of either the cell wall or the cell interior. In bacteria and fungi, they can both be cell components and metabolic products.

A large number of polysaccharides are in commercial use as, for example, materials for fibers, foods, industrial thickeners, blood plasma alternatives, blood anticoagulants, etc.
**HPLC**

In 1903, M. Tswett applied for the first time adsorption chromatography to the separation of plant pigments. The colored bands achieved in the separation of the pigments gave the technique the name of chromatography, from the Greek word chromatos, which means color.

Chromatographic techniques are widely used for analytical separation purposes. The mobile phase is either a liquid or a gas. The stationary phase may be a liquid coated inside of a capillary tube or on the surfaces of solid particles, or the solid particles may constitute the stationary phase themselves.

The separation is carried out by the different affinity of the solute and the mobile phase for the stationary phase.

There are several classes of chromatography:

1. Adsorption Chromatography: the stationary phase is a solid and the mobile phase is a liquid or a gas. Solutes are adsorbed on the surface of the solid particles.

2. Partition Chromatography: the stationary phase forms a thin film that coats the surface of solid particles. Solutes partitions between this liquid and the liquid mobile phase.

3. Ion-exchange Chromatography: the stationary phase is a resin, that has anions or cations attached. Solute ions of opposite charge are electrostatically attracted by the stationary phase.

4. Molecular Exclusion Chromatography: the liquid or gaseous mobile phase passes through a porous gel (stationary phase), that separates the molecules by size.

5. Affinity Chromatography: utilizes highly specific interactions between one kind of solute molecule and another molecule, covalently bonded to the stationary phase.
The mobile phase is called the eluent. When it comes out of the column, it is called the eluate. The speed of the mobile phase as it travels through the column is the volume flow rate. The retention time, defined for each kind of solute, is the time between the molecule is injected into the column and when it is eluted.

High Performance Liquid Chromatography achieves very high resolution by reducing the size of the particles that conform the stationary phase. To attain flow rates, between 0.5 and 5 ml/min., it is necessary to apply high pressure to force the liquid through the column, of the order of $10^6 - 10^7$ Pa.

Figure 17 shows a representative HPLC system.

![HPLC System Diagram](image)

Figure 17. HPLC System.

The pump must be capable of delivering a steady and reproducible flow, as fluctuations in the flow rate will lead to noise in the signal. Column and detector type will vary with specific applications. An ideal detector is sensitive to very low concentrations and its response is linear over the working range of concentration of the analyte. It must also be insensitive to the solvent, or mobile phase.
**Gel Permeation Chromatography**

It is also called molecular exclusion chromatography. It is used to separate molecules with respect to their size and finds applications in biochemistry and in polymer chemistry.

The stationary phase contains small pores which can be penetrated by small molecules, but not by large molecules. The volume available to these small molecules, is then higher than the available to bigger molecules (Figure 18). The elution volume of the unretained species is a measure of the void volume Vo. Small molecules which freely pass in and out of the pores have a greater elution volume, composed of the void volume and the intra particle volume or pore volume. Molecules of intermediate size will then permeate the pores at different elution volumes, Ve, which depend on their size.

For each stationary phase, there is a range for which a logarithmic relation between the molecular weight and the elution volume exists. A calibration curve has to be obtained running a series of standard of known molecular weight. However, molecules with the same molecular weight but different shapes exhibit different elution characteristics, because elution order is a function of effective molecular size, rather than weight. For example, the elution volumes of linear synthetic molecules would appear earlier than globular proteins of similar molecular weight. As a consequence of this, calibration curves must be determined for each type of sample.
Figure 18. GPC Column.

Large particles cannot penetrate the pores of the stationary phase and they are eluted before the small particles, that fit within the pores.
Ceramics

Raw Materials

*Boehmite* \( \gamma\text{-Al}(O)(OH) \)

The structure of the boehmia contains double sheets of octahedra with Al ions at their centers. These chains pack in layers joined by hydrogen bonding, as shown in Figure 19.

![Figure 19. Structure of Boehmite.](image)

Oxygens are at the vertices of each octahedron, and aluminum atoms are in the centre. Boehmite undergoes thermal decomposition through dehydration to yield \( \text{Al}_2\text{O}_3 \). The decomposition sequence is illustrated in Figure 20.
Figure 20. Transformation sequence for boehmite. (Alcoa Laboratories, 1987).

Saalfed (1960) found the sequence gamma-theta-alpha alumina when heating oriented aggregates of boehmite. According to Tertian and Papee (1958), delta-alumina occurs as an intermediate between gamma and theta. Wilson and Mc Connell found that the reaction sequence and kinetics depend on the properties of the original boehmite.

**Lepidocrocite**

Lepidocrocite is a layered compound, isostructural with boehmite. The structure consists of arrays of cubic close packing anions (O\(^2^-\) / OH\(^-\)) with Fe\(^{3+}\) ions occupying the octahedral interstices. Lepidocrocite is composed of double chains of Fe(O,O\(_2\))\(_6\) octahedra that share edges with adjacent double chains. Each chain is displaced by half with respect to its neighbor, forming corrugated sheets of octahedra. These sheets are separated by double rows of empty octahedral sites and held together by hydrogen bonds, as shown in Figure 21.
Figure 21. Arrangement of octahedral double chains in layers. Hydrogen bonds between layers are also shown.

Lepidocrocite transforms upon dry heating first to maghemite and then to hematite. The transformation to maghemite occurs at a temperature between 200°C and 280°C in air an under vacuum drops to 120°C. The layers of Fe(O,OH)₆ octahedra that form the lepidocrocite structure collapse perpendicular to their plane, inducing more corner and edge sharing and the formation and release of water. Dried meghemite transforms to hematite at temperatures from 370-600°C, depending on its origin and other ions content. A higher temperature is required because the transformation involves a charge in anion arrangement, from cubic close packing to hexagonal close packing.
Fabrication Processes

Sol-Gel Process

Ceramic membranes had had little application before the emergence of the sol-gel process, mostly because their relatively large pore size limited their use. The ceramic industry began to show interest in gels in the late sixties and early seventies. Controlled hydrolysis and condensation of alkoxides for preparation of multicomponent glasses was independently developed by several researchers. Ceramic fibers were made from metalorganic precursors on a commercial basis by various companies. However, the explosion of activity that continues today can be dated from the demonstration of Yoldas (1975) and Yamane et al. (1978) that monoliths could be produced by careful drying of gels. It turned out that the most important application of gels is in the field of thin films and fibers, as opposed to the preparation of bricks and windows, as initially intended.

Through the sol-gel process, membranes with pores in the nanometer range are obtained. Figure 22 illustrates the preparation route.

Figure 22. Sol Gel Process.
A colloidal suspension of particles in a liquid (sol) is formed with a precursor. This precursor consists of a metal or metalloid element surrounded by ligands, groups that do not contain another metal or metalloid. Alkoxyl radicals are commonly used as ligands. They are obtained by removing a proton from the hydroxyl on an alcohol. The application of metal alkoxides as precursors is due to their ability to undergo hydrolysis:

\[ M(OR)_4 + H_2O \rightarrow H - M(OR)_3 + ROH \]

where \( M \) is a metal and \( R \) is a proton or other ligand.

Depending on the amount of water and catalyst added, hydrolysis may go to completion \( M(OH)_n \) or stop while the metal is only partially hydrolyzed \( M(OR)_{4-n}(OH)_n \).

Two partially hydrolyzed molecules can link together in a condensation reaction that liberates a small molecule.

\[ (OR)_3M(OH) + OH - M(OR)_3 \rightarrow (OR)_3M - O - M(OR)_3 + H_2O \]

or,

\[ (OR)_3M(OR) + OH - M(OR)_3 \rightarrow (OR)_3M - O - M(OR)_3 + ROH \]

This type of reaction continues and a polymer is formed. The viscosity of the solution increases, which is an indication of the polymerization process. The sol is peptized by the addition of an acid, e.g. HCl or HNO₃, to form a stable suspension. During this process, if one molecule reaches macroscopic dimension, e.g. it extends throughout the solution, a gel is formed. Gelation can occur after a sol is cast into a mold, in which case it is possible to make
objects of any desired shape. Also, gelation can be produced by rapid evaporation of the solvent, as in the preparation of thin films or fibers. The structure of the gel is defined by the pH, concentration and nature of the ions used to stabilize the colloidal suspension.

Drying is a critical step in the fabrication process. The particles that conform the gel are very small, and high capillary forces are generated during drying that can result in cracks. The addition of an organic binder can solve this problem, by relaxing generated stresses. The ceramic is then sintered to stabilized its morphology. During this last step, the organic binder is removed by heating.

**Alumoxanes**

Alumoxane compounds were defined by Pasybkiewicz (1990) as species containing an oxygen bridge binding two aluminum atoms, Al-O-Al. They were first reported by Adrianov in 1958 as organically substituted aluminum oxygen macromolecules obtained from the reaction of aluminum alkoxides and siloxides.

The structure of alumoxanes was though of to consist of linear or cyclic chains. Apblett et al. (1992) redefined the structural view of alumoxanes and showed that they are not chains but three-dimensional cage compounds. For example, hydrolytically stable alumoxanes consist of an aluminum-oxygen core structure, shown in Figure 23, analogous to that found in the mineral boehmite, [Al(O)(OH)]n with an organic substituted periphery.
Figure 23. Structure of Alumoxanes

Based on this observation, a synthesis method directly from the mineral boehmite was developed (Barron et al., 1995).

Boehmite and a carboxylic acid were reacted in water to yield the respective carboxylate-alumoxane. The reaction produces a clear solution from which the alumoxane is obtained by drying. The carboxylic acids used as organic ligands are four:

1. Acetic Acid

\[
\text{O} \quad \text{C} \quad \text{O}
\]

2. Methoxyacetic Acid

\[
\text{O} \quad \text{C} \quad \text{O}
\]
3. Methoxyethoxyacetic Acid

\[
\text{OH} \quad \text{C} \quad \text{O} \\
\text{C} \quad \text{O} \quad \text{O} \\
\text{C} \quad \text{O} \\
\]

4. Methoxyethoxyethoxyacetic Acid.

\[
\text{OH} \quad \text{C} \quad \text{O} \\
\text{C} \quad \text{O} \quad \text{O} \\
\text{C} \quad \text{O} \\
\]

The carboxylate alumoxanes, prepared from the reaction of boehmite with carboxylic acids, are formed as a consequence of the cleavage of the boehmite structure (Figure 24).

Figure 24. Formation reaction of alumoxanes from boehmite.
The carboxylate groups are proposed to be bonded to the (100) plane of the boehmite-like core of the alumoxane. The IR spectra of the carboxylate alumoxanes contain bands at 1596-1586 and 1473-1466-1, consistent with a bridging mode of coordination of the carboxylate to the boehmite core. (Figure 25).

![Diagram of organic acid bond to boehmite structure](image)

Figure 25. Organic acid bond to the boehmite structure.

Applications for alumoxanes are possible in a variety of fields and include uses as ceramic precursors, additives in paints and coatings, antiperspirants and supports for metal colloids. In the 1960's and throughout the 1980's their use as catalysts in the polymerization of propylene oxide, epoxides, butadiene and propylene was extensively studied.

We are interested in their value as preceramics. The alumoxanes are indefinitely stable under ambient conditions and are adaptable to a wide variety of processing techniques, including infiltration, dip coating, spin-coating and spray coating onto various substrates.

Concentrated mixtures of the alumoxanes with water form rigid gels. Carboxylate alumoxanes decompose above 180°C to give amorphous alumina. Firing above 900°C results in the formation of a mixed phase γ-Al₂O₃ and α-Al₂O₃ as expected form the transformation sequence of aluminas, and they are converted to α-alumina above 1200°C.
Powder Consolidation Methods

Mechanical compaction of dry or semidry powders in a die is one of the most widely used forming operations in the ceramic industry. A drawback of this technique is that, in general, the applied pressure is not transmitted uniformly due to friction between the particles and the walls of the die, resulting in density variations that limit the degree of packing uniformity that can be achieved. Thus, it provides far less control than the colloidal techniques on the properties of the pre-fired ceramic or green body.

Plastic forming methods, such as extrusion and injection molding, have also been extensively used in the traditional ceramic industry. A mixture of the ceramic powder and additives is deformed plastically through a nozzle or in a die to form the desired shape. These methods are similar to those used in the plastics industry.

The following table (Table 4) summarizes the common methods used to consolidate ceramic powders to form the green body. The method selected will depend on the complexity of the shape and size required. Simple shapes can be made by uniaxial pressing, but other forming processes are needed to manufacture more complex ones.
<table>
<thead>
<tr>
<th>FORMING METHOD</th>
<th>FEED MATERIAL</th>
<th>SHAPE OF THE POWDER FORM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry or semidy pressing</td>
<td>Powder or free flowing granules</td>
<td>Small simple shapes</td>
</tr>
<tr>
<td>Die compaction</td>
<td>Powder or free flowing granules</td>
<td>Small simple shapes</td>
</tr>
<tr>
<td>Isostatic pressing</td>
<td>Powder or fragile granules</td>
<td>Larger, more intricate shapes</td>
</tr>
<tr>
<td>Casting of a slurry</td>
<td>Free-flowing slurry with low binder content</td>
<td>Thin intricate shapes</td>
</tr>
<tr>
<td>Slip Casting</td>
<td>Free-flowing slurry with high binder content</td>
<td>Thin sheets</td>
</tr>
<tr>
<td>Tape casting</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deformation of a plastic mass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extrusion</td>
<td>Moist mixture of powder and binder solution</td>
<td>Elongated shapes with uniform cross section</td>
</tr>
<tr>
<td>Injection molding</td>
<td>Granulated mixture of powder and solid binder</td>
<td>Small intricate shapes</td>
</tr>
</tbody>
</table>

Table 4. Feed materials and Shapes of the consolidated Powder Form for the Common Ceramic Forming Methods (Rahaman, 1995).

Additives play a vital role in many forming processes. Although sometimes present in very low concentration, they help to control the characteristics of the feed and the packing uniformity of the consolidated body. They can be classified with respect to their function in four categories:
1. Binders: in small concentrations, serve to provide bridges between particles and strengthen the green body; when used in high concentrations in plastic forming methods, they provide plasticity to the feed material. Most binders are organic long-chain polymer molecules with side groups attached: vinyls, acrylics and polyethylene oxides.

2. Plasticizers: they increase the flexibility of the green body; they are usually lower molecular weight organics: glycols, glycerol, phthalates.

3. Dispersants or deflocculants: they stabilize the slurry by increasing the repulsion between particles; common dispersants used in water are sodium silicate, sodium carbonate tetrasodium pyrophosphate.

4. Lubricants: they reduce the friction between particles and between particles and the walls of the die; common examples are steric acid, stearates and various waxy substances.

Traditional ceramic preparation methods have been extensively applied to the preparation of ceramic supports for asymmetric membranes. Das et al. (1996) fabricated alumina filters by the tape casting technique. The filters were disc shaped with pore size in the range of 100 to 700 nm. They found that the initial particle size was the most important factor in the determination of the pore size of the filter. Avci et al. (1996) reported their work on microfiltration supports from alumina powders. Avci prepared substrates by uniaxial dry-pressing in disc shapes with a diameter of 40 mm and a thickness of 2.5 mm. The obtained supports have an average pore diameter of 90 to 100 nm. Schaep et al. (1999) fabricated α-Al₂O₃ discs by uniaxial pressing to use as support in the preparation of nanofiltration membranes by the sol-gel and dipping technique. The discs reported were 25 mm in diameter and had a maximum pore size of 200 nm.
Thin Film Coating Technologies

The application of inexpensive coatings to the surface of solid bodies represents a simple and economical way to obtain new materials for specific applications. To this date, the sol-gel approach is by far the most widely used technology to produce thin ceramic films on substrates.

Two main techniques have been used to produce the film: dip coating and spin coating. In dip coating, the substrate is put in contact with the solution, lowering it and withdrawing at a certain speed. It is the most widely used technique, because it does not require any special apparatus. The contact angle between the solution and the surface of the object must be small, so that the solution wets and spreads over the surface. The thickness of the film obtained depends on the viscosity of the solution and speed of withdrawal. Films of 1 μm can be deposited. Spin coating is the process in which the solution is dropped onto the object spinning at high speed. Only one side of the object can be coated. Furthermore, edge effects can appear if the substrate is not symmetric. The thickness of the deposited film varies inversely with the angular velocity of the object, but it is also dependent on the solution viscosity (Rahaman, 1995).

Sintering

The firing process is the heat treatment of the green body with the objective of strengthening mechanical properties and fixing its shape. The spontaneous strengthening of fine-grained porous bodies by the effect of high temperatures is called sintering. This process involves shrinking and densification.

The driving force in sintering is the tendency to reduce surface area; the free energy of the system decreases as a result of elimination of the solid-gas interface. In a sense, the
phenomenon is analogous to the joining of water drops through effect of surface tension. The connecting neck which is first formed widens until the two drops become one. The low viscosity of water allows for deformation and the process is fast; in the case of solid particles, energy in the form of high temperature is required for the deformation to take place, and even then, the joining of the particles is slow and incomplete.

The sintering of pure solids happens at temperatures of 80-90% of their melting point. For example, the melting point of alumina is 2054°C, but sintering starts at 1600-1800°C for particles in the micron range, and even at lower temperatures for smaller particles. Figure 26 illustrates the sintering process of 20 μm alumina particles after heating at 1750-1840°C (Bartuska and Hlavac, 1961).

At the beginning, the particles have one point of contact, from which an expanded bond area or neck is formed. Later, the particles enclose a spherical pore that tends to contract by the effect of the surface tension. If the particles allow for deformation, the pore will contract until the pressure of the gases trapped inside the pore is equal to the contracting force of surface tension. After that point, the pore will continue to contract but at a much lower rate, dictated by the rate at which the gasses are released from the pores by diffusion. Ideally it is possible to continue sintering until the final product of sintering is a dense body, where all the pores have been eliminated. In reality, the ceramic will always exhibit some porosity.

The firing schedule is typically composed of a gradual heating, a dwell time at the highest temperature, when sintering takes place, and a controlled cooling. The rate of heating is determined by the need for uniform heating in samples with low thermal conductivity and some supplementary processes, such as decomposition of hydrates and carbonates and polymorphic transformations. The time at the maximum temperature is defined by the kinetics of the sintering process. The rate of cooling is also limited by the formation of stress on the surface of the ceramic.
Figure 26. Sintering of spherical Al$_2$O$_3$ particles (Bartuska and Hlavac, 1961).
Chapter 3

Methods and Materials

Commercial membranes investigated as supports

Two commercial membranes have been studied for potential use as supports for asymmetric membranes. Anodisc membranes (Whatman) consist of Anopore membrane discs 46 mm in diameter bonded to an annular polypropylene ring acting as support material. Anopore is an aluminum oxide membrane with a honeycomb-like structure. Anodiscs filters of pore sizes 0.2 μm, 0.1 μm and 0.01 μm were studied. The average thickness of these membranes is 60 μm. The other support material considered was an α-alumina ceramic filter (Refracton Technologies Corp.). These filters were prepared by sol-gel synthesis and calcinated at 1400°C. It was not possible to obtain a precise specification from the manufacturer because the product was still in the development phase. Further characterization was performed in our laboratory and is presented in chapter 4.
Preparation of Supports

Alumina supports were prepared by uniaxial pressing. High purity calcinated alumina (Catalox Sba 150, Condea Vista) was used as the starting material. Table 5 shows the specification for the alumina.

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>SPECIFICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Size</td>
<td></td>
</tr>
<tr>
<td>&lt; 20 µm</td>
<td>20.0 wt%</td>
</tr>
<tr>
<td>&lt; 45 µm</td>
<td>50.0 wt %</td>
</tr>
<tr>
<td>&lt; 90 µm</td>
<td>85.0 wt %</td>
</tr>
<tr>
<td>&lt; 125 µm</td>
<td>90.0 wt%</td>
</tr>
<tr>
<td>&gt; 1000 µm</td>
<td>0.0 wt %</td>
</tr>
<tr>
<td>Surface Area</td>
<td>138 - 158 m²/g</td>
</tr>
<tr>
<td>Phase Composition</td>
<td></td>
</tr>
<tr>
<td>Gamma/ Delta</td>
<td>97.5 %</td>
</tr>
<tr>
<td>Alpha</td>
<td>0.0 %</td>
</tr>
</tbody>
</table>

Table 5. Properties of the alumina powder used in the preparation of supports.

A stainless steel cylindrical die was filled with alumina powder and compacted using a hydraulic press to form the green body. The die was 60 mm in diameter and 6 mm deep. The maximum force applied was 15 tons. for a period of 1 minute. The green body was then fired at 1400 °C for 40 hours.
**Preparation of Alumoxanes**

Acetic Acid Alumoxanes were prepared in the laboratory from powdered boehmite (Condea Vista) with the specifications shown in Table 6. Boehmite (100 g.) was mixed with Millipore water (800 ml.) and acetic acid glacial (Aldrich, 80 ml). The suspension was stirred for 30 minutes to allow for the reaction to take place and then centrifuge at 16,000 rpm for an hour to remove unreacted boehmite. The solution was let to dry at room temperature for the time needed until all the water was evaporated.

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>SPECIFICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Size</td>
<td></td>
</tr>
<tr>
<td>&lt; 45 µm</td>
<td>50.0 wt %</td>
</tr>
<tr>
<td>&gt; 90 µm</td>
<td>30.0 wt %</td>
</tr>
<tr>
<td>Surface Area</td>
<td>220 m² / g</td>
</tr>
</tbody>
</table>

Table 6. Specifications for boehmite.

**Preparation of un-supported and supported membranes**

Unsupported acetic acid alumoxane derived membranes were prepared by dissolving 2 grams of AA-alumoxane in 20 ml of water. The suspension was dried on a Petri dish to form a glassy, transparent material which was later fired to yield the alumina ceramic.
Ceramic filters used as supports were coated with an AA-alumoxane solution by the dip coating technique. This technique was chosen because it allowed for the formation of a thin coating layer, it is simple and it does not require any special equipment. One side of the supports was dipped into a 1% AA-alumoxane solution until all the surface was wet and then it was quickly withdrawn from the liquid. The excess of water was removed and then the coated support was let to dry at room temperature.

The coated supports were then fired under a prescribed progression of temperatures. The firing program is presented in Figure 27. For the membranes prepared at 600°C, the firing scheduled ended after the first plateau.

Figure 27. Firing Schedule.
**Preparation of Ferroxanes**

Ferroxanes and ferroxane-derived membranes were prepared by Jerome Rose and his research group at the Centre Européen de Recherche et d'Enseignement de Géosciences de l'Environnement (CEREGE), Aix-en-Provence, France. Lepidocrocite (2 grams.) was reacted with 2.275 ml of acetic acid, which corresponds to a molar ratio of 2/1 (acetic acid / lepidocrocite). The solution was refluxed at 80°C overnight and centrifuged at 3000 rpm for one hour.

Ferroxane-derived membranes, both supported and unsupported, were prepared in the same way as alumoxane-derived membranes.

**X-ray Powder Diffraction**

The X-rays analysis was performed by Cyrille Magnetto at the Centre Européen de Recherche et d'Enseignement de Géosciences de l'Environnement (CEREGE), Aix-en-Provence, France. The equipment used was a Philips PW1730 diffractometer, with an Cobalt anode (40kV and 40 mA).

**AFM**

Samples were imaged using a Nanoscope IIIa Scanning Probe Microscope, in tapping mode AFM (Digital Instruments). TappingMode Etched Silicon Probes (TESP) were used with a pyramidal shape and end radius of 5-10 nm (Digital Instruments). The tip half angles are 17° side, 25° front and 10° back (Figure 28). Very little sample preparation is required in this
technique: small pieces of sample were attached to 15mm magnetic discs (Digital Instruments) with black carbon double sided tape.

Figure 28. TESP tip angles.

**SEM**

SEM images were taken using a JEOL JSM 5300 Scanning Microscope. The samples were prepared as follows: pieces of membranes were attached to aluminum studs in different positions to allow for the imaging of surfaces, cross sections, etc. The samples were sputtered with gold to create a conducting surface.
Nitrogen Gas Adsorption/Desorption

Nitrogen adsorption/desorption was used to measure surface area and pore size distribution (Coulter SA 3100 analyzer). The SA 3100 analyzer uses the static fully equilibrated method. In this method, discrete data points are obtained as gas pressures are equilibrated before readings are recorded. The volume of adsorbate gas retained by the sample is calculated from the pressures measured at each data point. The volume of each dose of gas is constant. The volume of the sample tube not occupied is an unknown at the beginning of the analysis, which is called the freespace. Helium gas is used to measure the free space in the sample cell. A reference cell is used to compare changes in pressure in the sample cell. Both reference and sample cells are kept at 77 K, by immersion in boiling nitrogen. The mass of sample required varies with its surface area; for our samples, it ranged between 0.1 and 0.3 grams. Each sample was outgassed with a nitrogen purge prior to the experiment for 10 hours at 150 C.

Average pore sizes were calculated from the adsorption branch of the isotherm using the following equation:

$$ dp = \sum \frac{V_i}{V_T} * dp_i $$

where

dp is the average pore diameter of the sample,
Vi is the volume of the pores in the i\textsuperscript{th} pore size range,
V_T is the total volume of the sample, and
di is the pore size of the i\textsuperscript{th} pore size range.

The standard deviation, S, of the pore size distribution was calculated as
\[ S = \sqrt{\sum \left[ \frac{V_i}{V_T} \ast (dp - dpi)^2 \right]} \]  

(21)

**Permeability Determinations**

Pure water flux was measured for the supports and coated supports to calculate their permeability. The samples were glued using silicone adhesive to plastic rings to adapt their size to the filtration cell. The effective filtration area was \(1.61 \times 10^{-3} \text{ m}^2\) in all cases. The experiments were conducted in a dead end filtration cell (Amicon, model 8200). Pressure was provided by a zero air tank connected to the cell and a regulator was used to set the it to a constant value (10 psi). The temperature was 25°C for all the experiments.

![Diagram](image)

Figure 29. Experimental set up for permeability measurements.

The permeate was collected in a graduated cylinder at atmospheric pressure, so that the pressure at the end of the regulator is equal to the transmembrane pressure (Figure 29).
Permeate volume was recorded over time and the total volume of permeate was plotted versus time. It results in a straight line, the slope representing the flux $J$. Given that the area, thickness of the filter, transmembrane pressure, flux and viscosity of water were known, permeability was calculated using Darcy's law and assuming cylindrical pores (Poiseuille's flow).

**MWCO**

The MWCO experiments are performed in two parts. First, a test solution is filtered. Permeate and feed samples obtained in the first part of the experiment are analyzed by GPC, in order to determine their molecular weight distribution.

The experimental set up for the filtration is depicted in Figure 30.

![Experimental setup for MWCO determinations](image)

Figure 30. Experimental set up for MWCO determinations.
The test solution was prepared with the following concentrations of dextran fractions (Sigma Chemical Co.): 0.25 wt% T-10 (average molecular weight 10,500), 0.10 wt% T-40 (avg. MW 37,500), 0.10 wt% T-70 (average MW 69,800) and 0.20 wt% T-500 (average MW 413,000). Sodium Azide (99%, Aldrich) was added at a concentration of 0.05 wt% to prevent bacterial growth and sodium chloride (NaCl) 0.05 M to prevent interaction between molecules and surfaces. Ultrapure water was used in all the experiments (10 MΩ quality).

The dextran solution was pumped at a constant flow rate of 105 ± 5 ml/ min. by the diaphragm pump (DP). A flowmeter (FM1) was used to monitor continuously the flow and a pulse dampener was added at the pump outlet to minimize flow fluctuations into the cell. Samples prepared as explained for permeability measurements were placed in a stirred ultrafiltration cell (Amicon, Model 8200). The cell was modified to allow for recirculation of the feed. A hole was drilled in the top of the cell to insert a 1/8” stainless steel tube, used as inlet for the feed. The existing fitting was used as exit for the feed stream.

A valve and pressure gage at the feed exit of the cell allowed for transmembrane pressure control. The pressure at the gage was set at 7 ± 0.5 psi. A peristaltic pump (PP) added at the permeate line and a second flow meter (FM2) was used to ensure that the permeate flow rate was kept below 0.15 ml/min. to avoid deformation effects of the macromolecules. The system ran for 30 min. under the previously described conditions before a permeate sample was collected. A sample of the feed was also taken each time the filtrate was sampled.

Feed and permeate samples were analyzed by GPC. A HPLC system (Waters 717plus Autosampler, Waters 600E System Controller) was used with a GPC column (TosoHaas G4000PWXL). Ultrapure water was used as solvent. Calibration curves (molecular weight vs. elution time) were obtained by running each dextran fraction separately. The peak was assumed to correspond to the average molecular weight given by the manufacturer.
The flow rate through the column was set to 1 ml/min. The eluate was collected every milliliter with a fraction collector (Waters). Fifteen fractions were collected during each run, corresponding to the first fifteen minutes of the run. The concentration of dextran in each fraction was determined measuring organic carbon concentration, using a Total Organic Carbon Analyzer (Shimatzu, TOC 5050A). In order to attain the volume needed to run the samples in the TOC analyzer, two milliliters of ultrapure water were added to each fraction, resulting in a dilution factor of three. Calibration curves relating organic carbon and dextran concentration were previously obtained for each dextran fraction, between 10 ppm and 1,000 ppm. The relationship was found to be linear, and the slope for all different dextran fractions was within 2%. An average coefficient was used to convert organic carbon to dextran concentrations for the fractions mixture in the test solution.

Three HPLC runs were performed with each sample and each fraction was analyzed three times by the TOC analyzer.

The organic carbon content was plotted as a function of fraction elution time to obtain the elution curves. All the organic carbon measured is assumed to be due to dextrans, although several interferences were present. Carbon dioxide dissolution was minimized by adding a drop of HCl to the samples. The most important interference came from the organics used as solvents by the manufacturer to ship the GPC column. Ultrapure water was run through the column until the TOC levels were below 1.000 ppm, but some background TOC concentrations were always detected. The dilutions are another source of error, since extremely low concentrations as in the case of the permeate, were diluted three times, and its value fell near the background level, making it very difficult to accurately determine the dextran concentration.
Results and Discussion

Supports Materials Investigated

Anodiscs (TM)

To evaluate their potential application as alumoxane membrane supports, anodiscs filters were exposed to the firing conditions required to prepare the membranes. Filters fired to 600 °C showed no visible change. When fired at 800 °C, they curled up.

Anodiscs surface was investigated using AFM and SEM images. Figure 31 shows the surface of an anodisc filter as they are sold. Figure 32 is a closer look, where the rather low surface porosity is apparent.
Figure 31. SEM image of an Anodics filter.

Figure 32. SEM image of an Anodics filter.
Fragments of filters fired to 800°C were examined using both techniques. While AFM scans showed no apparent change in the pore structure (Figures 33 and 34), when imaged by SEM some cracks in the surface were detected (Figure 35). Figure 36 is a detailed look at a pore that collapsed during firing. Although the crack does not seem to go all the way to the other side of the filter, it is reasonable to assume that at higher temperature, 1000°C, and longer firing times it will grow bigger and eventually run through the whole thickness of the membrane. The thermal resistance of this filter is then much lower than required for the application as support materials, and therefore they were not considered further.

However, one interesting conclusion can be drawn about the applicability of AFM and SEM. While AFM scans are useful to investigate at surface features at very low scales in rather homogeneous surfaces, SEM images proved to provide a better overall characterization of the surface, specially when one small section may not be representative of the whole.

![AFM scan of an Anodisc filter.](image)

Figure 33. AFM scan of an Anodisc filter.
Figure 34. AFM scan of an Anodisc filter fired at 800°C.

Figure 35. SEM image of an Anodics filter fired at 800°C.
Figure 36. SEM image of an Anodics filter fired at 800°C.

α - Alumina Filters

α-Alumina filters were characterized in the lab to evaluate their potential as membrane supports. The pore size distribution was measured by nitrogen adsorption/desorption. Figure 37 shows the pore volume distribution as a function of average diameter. The average values are summarized in Table 7.
Figure 37. Pore volume distribution for $\alpha$-alumina supports as determined by N$_2$ adsorption.

<table>
<thead>
<tr>
<th></th>
<th>Average Pore size (nm)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run1</td>
<td>109.5581</td>
<td>47.1664639</td>
</tr>
<tr>
<td>Run2</td>
<td>101.303469</td>
<td>52.9727049</td>
</tr>
<tr>
<td>Average</td>
<td>105.430785</td>
<td>50.0695844</td>
</tr>
</tbody>
</table>

Table 7. Volume-average pore size for $\alpha$-alumina supports.

The permeability of the $\alpha$-alumina filters was measured for 11 samples. The values ranged between 27.4 nm$^2$ and 36.5 nm$^2$; the average permeability was 33 nm$^2$ and the standard
deviation 3.2 nm². The thickness of the filter vary between 1 mm to 1.8 mm, which yielded a reasonable good flow.

MWCO experiments were also conducted with these samples but no conclusive results could be found. The range of applicability of the MWCO test is determined by the size of the molecules in the test solution. Dextran are commercially available from 10,000 grams and 500,000 grams average molecular weight. Applying the correlation given by Worch (1993), the size of these molecules is between 2.68 nm and 21.36 nm. Therefore, the method will only be valid for membranes with pore sizes in that range. The MWCO experiments showed that the filter permit the pass of all molecules in the test solution, as expected from the pore size distribution measurements.

Coating of supports

The supports were coated with acetic acid alumoxane solutions by dip coating. This technique proved to be effective in achieving membranes of low and uniform thickness, if care was taken to assure that all the surface of the support was wetted by the coating solution. Another coating technique used was the application of the solution on top of the support with a syringe. The disadvantages of this approach are that it is very difficult to obtain a layer of the thickness achieved by dip coating, and it is practically impossible to distribute the alumoxane particles evenly throughout the surface of the support.
Characterization of Unsupported Membranes

Unsupported membranes were prepared in order to run nitrogen adsorption experiments, SEM imaging and X-ray diffraction analysis. These membranes were fired at different temperatures ranging from 600 °C to 1400 °C to study the dependence of their properties on the firing temperature.

Nitrogen Adsorption/ Desorption

The surface area of the samples showed a small decline up to a firing temperature of 1000 °C; at higher temperatures, it decreases dramatically due to the formation of grains and the transformation to α-alumina. The pore volume shows a similar trend. While the pore size increases at temperatures higher than 1000 °C, the pore volume and the surface area undergo an important reduction, which suggests that the ceramic has lost its original high porosity. The results are summarized in Table 8. The correlation coefficient is in all cases higher than 0.999. The lowest values for the correlation coefficient occur in analysis of samples fired at 1300°C and 1400°C because their pore volume and surface area are lower and thus the accuracy is compromised. The focus of this work is to prepare and characterize ultrafiltration membranes, and so these last two samples were of little interest in the project.
<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>BET Surface Area m²/g</th>
<th>Corr. Coef.</th>
<th>Pore Volume ml/g</th>
<th>Average Pore Size nm</th>
<th>Standard deviation nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>208.91</td>
<td>0.99990</td>
<td>0.3307</td>
<td>6.48</td>
<td>5.65</td>
</tr>
<tr>
<td>700</td>
<td>216.27</td>
<td>0.99995</td>
<td>0.3902</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>800</td>
<td>194.06</td>
<td>0.99995</td>
<td>0.3823</td>
<td>8.39</td>
<td>10.44</td>
</tr>
<tr>
<td>900</td>
<td>167.99</td>
<td>0.99998</td>
<td>0.3717</td>
<td>9.15</td>
<td>9.88</td>
</tr>
<tr>
<td>1000</td>
<td>119.63</td>
<td>0.99996</td>
<td>0.3157</td>
<td>10.47</td>
<td>5.54</td>
</tr>
<tr>
<td>1030</td>
<td>56.061</td>
<td>0.99999</td>
<td>0.1909</td>
<td>22.59</td>
<td>24.85</td>
</tr>
<tr>
<td>1050</td>
<td>18.816</td>
<td>0.99999</td>
<td>0.1573</td>
<td>66.66</td>
<td>34.24</td>
</tr>
<tr>
<td>1070</td>
<td>6.660</td>
<td>1.00000</td>
<td>0.0655</td>
<td>88.17</td>
<td>30.54</td>
</tr>
<tr>
<td>1100</td>
<td>24.995</td>
<td>0.99999</td>
<td>0.1341</td>
<td>65.18</td>
<td>42.16</td>
</tr>
<tr>
<td>1200</td>
<td>5.294</td>
<td>0.99993</td>
<td>0.0148</td>
<td>129.44</td>
<td>60.20</td>
</tr>
<tr>
<td>1300</td>
<td>3.931</td>
<td>0.99976</td>
<td>0.0093</td>
<td>-</td>
<td>47.03</td>
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<tr>
<td>1400</td>
<td>1.477</td>
<td>0.99934</td>
<td>0.0042</td>
<td>-</td>
<td>42.22</td>
</tr>
</tbody>
</table>

Table 8. Surface area, pore volume and average pore size of AA derived membranes fired at temperatures from 550 °C to 1400°C.

Figure 38 and Figure 39 display the variation of surface area and pore volume with temperature. The average pore size as a function of firing temperature is showed in Figure 40. It can be observed that there is very little variation until 1000°C, and then both the pore sizes and the standard deviation increases substantially. The standard deviations depicted in this chart correspond to the standard deviation of the pore size distribution and they are not an indication of experimental error. The gradual transformation to α-alumina and the subsequent collapse of the pores is responsible for the wider distribution at higher firing temperatures.
Figure 38. Surface area of AA derived membranes as a function of firing temperature.

Figure 39. Pore Volume of AA derived membranes as a function of firing temperature.
Figure 40. Average pore size of AA derived membranes as a function of firing temperature.

SEM

The membranes were imaged by SEM to identify surface features that may appear at each firing temperature and to confirm the pore sizes measured by nitrogen adsorption.

Figures 41 through 48 show the changes in surface topology as the firing temperature is increased. From 600°C to 900°C (Figures 41 and 42) no major changes are detected; when observed at higher magnification (Figures 47 and 48) they present the same structure of small particles sintered together, although pores may be slightly bigger in the membrane fired at
900°C, as expected from nitrogen adsorption measurements. At 1100°C (Figure 43), some transformation to α-alumina begin to occur, and the starting growth of grains are observed. This new morphology is clearly noticed in the samples fired at higher temperatures (Figure 44, 45 and 46) where the small particles have all sintered together and cause the collapse of the small pores, resulting in the formation of larger, elongated pores. These findings corroborate the pore sizes obtained by nitrogen absorption; rather unchanged structure up to 1000°C - 1100°C, when the transformation to α-alumina begins, followed by the formation of much larger pores.

Figure 41. SEM image of AA derived membrane fired to 600°C.
Figure 42. SEM image of AA derived membrane fired to 900°C.

Figure 43. SEM image of AA derived membrane fired to 1100°C.
Figure 44. SEM image of AA derived membrane fired at 1200°C.

Figure 45. SEM image of AA derived membrane fired at 1300°C.
Figure 46. SEM image of AA derived membrane fired at 1400°C.

Figure 47. SEM image of AA derived membrane fired at 600°C.
Figure 48. SEM image of AA derived membrane fired at 900°C.

AFM

The pore sizes measured by other techniques in this work were compared to the values reported by Diane Bailey (Department of Environmental Science and Engineering, Rice U.). She performed AFM scans and determined pore sizes by means of the section analysis tool available in the AFM software. Figure 47 shows a 200 nm scan of AA derived membrane; the openings between grains are visible but the size of the pores cannot be estimated. The section analysis (Figure 48) displays pores between 14 nm and 21 nm in diameter, higher than the values obtained by nitrogen adsorption. The overestimation of pore sizes by AFM is in part due to the geometry of the pores. The tip only detected the size of the entrance of the pore, while the diameter of the neck of the pore can be considerably smaller.
Figure 47. 200 nm AFM scan of AA derived membrane. (scanned by D. Bailey)

Figure 48. AFM section analysis of AA derived membrane. (scanned by D. Bailey)
X-ray powder diffraction

Acetic acid alumoxane membranes were sintered at temperatures of 600°C, 800°C, 900°C, 1000°C and 1100°C and analyzed by X-ray powder diffraction to determine the phase of the material at each firing temperature. The results are presented in Table 9.

<table>
<thead>
<tr>
<th>Sintering Temperature</th>
<th>Phase</th>
<th>Mineralogical File Number (JCPDS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600 °C</td>
<td>γ-Al₂O₃</td>
<td>29-0063</td>
</tr>
<tr>
<td>800 °C</td>
<td>γ-Al₂O₃</td>
<td>29-0063</td>
</tr>
<tr>
<td>900 °C</td>
<td>γ-Al₂O₃</td>
<td>29-0063</td>
</tr>
<tr>
<td>1000 °C</td>
<td>θ-Al₂O₃</td>
<td>35-0121</td>
</tr>
<tr>
<td>1100 °C</td>
<td>α-Al₂O₃ ; traces of θ-Al₂O₃</td>
<td>05-0712</td>
</tr>
</tbody>
</table>

Table 9. X-ray powder diffraction analysis for acetic acid alumoxane membranes.

The transformation sequence is similar to that of boehmite. The results are also in good agreement with the nitrogen adsorption data, in that the important change in pore size and surface area observed corresponds to the transformation to α-Al₂O₃, and this transformation involves change in the crystallographic structure. Figures 49 to 53 show the diffraction patterns for the samples.
Figure 49. Diffractogram of an alumoxane derived membrane fired at 600°C
phase gamma-Al2O3
Mineralogical file number (JCPDS) = 29-0063

Figure 50. Diffractogram of an alumoxane derived membrane fired at 800°C
phase gamma-Al2O3
Mineralogical file number (JCPDS) = 29-0063

Figure 51. Diffractogram of an alumoxane derived membrane fired at 900°C
phase gamma-Al2O3
Mineralogical file number (JCPDS) = 29-0063

Figure 52. Diffractogram of an alumoxane derived membrane fired at 1000°C
phase theta-Al2O3
Mineralogical file number (JCPDS) = 35-0121

Figure 53. Diffractogram of an alumoxane derived membrane fired at 1100°C
phase alpha-Al2O3
Mineralogical file number (JCPDS) = 05-0712
Characterization of Supported Membranes

SEM

SEM images were obtained to investigate the order of magnitude of the coating layer. For comparison purposes, all of the following images were performed on samples fired at a maximum temperature of 1000°C.

Figures 54 to 56 are images of cross sections of α-alumina supports coated once with acetic acid alumoxane by the dip-coating technique. The scans were performed by Christopher Jones, Department of Chemistry, Rice University.

The membranes exhibit a uniform and smooth surface, the thickness of the active membrane layer not exceeding a few micrometers. The difference in grain size between the support and alumoxane derived membrane is evident.

![SEM image of an acetic acid alumoxane derived membrane (cross section).](a)

Figure 54. SEM image of an acetic acid alumoxane derived membrane (cross section).
Figure 55. SEM image of an acetic acid alumoxane derived membrane (cross section).

Figure 56. SEM image of an acetic acid alumoxane derived membrane (cross section).
The top surface of the membrane layer was also imaged in order to identify defects in the coating process or cracks that may occur during sintering. Cracks were observed in some samples, where the membrane layer is open and exposes the support material (Figures 57 and 58). This feature results in a defective membrane, as the solute being filtered passes through the crack without restrictions. While performing a molecular weight cut off experiment, the presence of cracks in the membrane is easily detected by a drastic increase in the cut off value.

Figure 57. SEM image of a crack on the surface of a acetic acid alumoxane derived membrane layer on a α-alumina support.
Figure 58. SEM image of a crack on the surface of a acetic acid alumoxane derived membrane layer on a \( \alpha \)-alumina support, closer view. The bigger particles that form the support can be seen and compared to the much smaller alumoxane particles.

Permeability

The permeability of the \( \alpha \)-alumina supports was determined before and after coating with the alumoxanes. The supports were found to have a permeability between 27.43 \( \text{nm}^2 \) and 36.55 \( \text{nm}^2 \), with a mean of 32.97 \( \text{nm}^2 \) and a standard deviation of 3.23 \( \text{nm}^2 \). After coating, the permeability of the samples was measured again. Its value ranged between 22.17 \( \text{nm}^2 \) and 27.84 \( \text{nm}^2 \); the mean was 25.00 \( \text{nm}^2 \) and the standard deviation 2.39 \( \text{nm}^2 \).

Although these measurements adequately describe the flux capability of the samples prepared, they can not be taken as characteristic of the alumoxane derived membranes, because
they are dependent on the permeability of the support used. It would be more useful to have a determination of the permeability of the active layer alone, rather than of the asymmetric membrane as a whole.

The resistance of an asymmetric membrane, $R_t$, can be regarded as the sum of two different resistance in series: the resistance of the active membrane layer, $R_m$, and that of the support material, $R_s$.

$$R_t = R_s + R_m \quad (22)$$

Also, Darcy's law can be expressed in terms of membrane resistance or permeability, in which cases it takes the following forms:

$$J = \frac{\Delta P}{\mu \times R} \quad (23) \quad J = \frac{k \times \Delta P}{\mu \times l} \quad (24)$$

and therefore the relationship between membrane resistance and permeability is

$$R = \frac{l}{k} \quad (25)$$

Equation 22 can be re-written as

$$\frac{l_T}{k_T} = \frac{l_S}{k_S} + \frac{l_m}{k_m} \quad (26)$$
where

$l_T$ and $k_T$ are the total thickness of the asymmetric membrane and its permeability,

$l_S$ and $k_S$ are thickness and permeability of the support and

$l_m$ and $k_m$ are those of the membrane layer, respectively.

The permeability and thickness of the support and of the asymmetric membrane are known from the permeability experiments; the thickness of the membrane layer was estimated by SEM imaging of cross sections; we can then calculate $k_m$, the permeability of the alumoxane material.

From Equation 26, we can solve for $k_m$

$$k_m = \frac{l_m}{\left(\frac{l_T}{k_T} - \frac{l_S}{k_S}\right)} \quad (27)$$

The average thickness of the support is 1.56 mm and the thickness of the membrane layer is estimated in 3 μm; the thickness of the asymmetric membrane is assumed to be equal to that of the support, as the addition due to the membrane layer is three orders of magnitude smaller and thus, not significant. The calculated permeabilities for the alumoxane layer varied between 0.11 nm$^2$ and 0.75 nm$^2$, with an average of 0.32 nm$^2$. These values are lower than those reported by D. Bailey (1997), who measured the permeability of small unsupported alumoxane derived membrane fragments epoxyed to aluminum foil disks. She reported permeabilities ranging from 0.36 nm$^2$ and 0.52 nm$^2$, and an average value of 0.44 nm$^2$, 37% higher than those calculated in this work.

Sources of error can be the membrane surface area and thickness of the membrane fragments. Errors in the present work can be attributed to irregularity in the thickness of the
support, for which an average value was taken and the estimation of thickness of the active layer, that can also vary along the surface. The surface area was carefully measured and it was equal to the area of the supports, constant throughout the experiments. The pressure was kept constant and it is unlikely that it may introduce significant error. To effectively reduce the uncertainty in the experiment, supports with uniform properties (thickness, grain size) are needed. Border irregularities observed in some of the supports also negatively affect the permeability determinations, due to uneven deposition of alumoxane particles by dip-coating that results in differences in thickness of the active layer.

Molecular Weight Cut Off

Before performing the MWCO experiments, the test molecules were characterized by GPC. The peak of the elution curve (Figures 59 through 62) was assumed to correspond to the average molecular weight provided by the manufacturer. The molecular weight distribution was investigated for each fraction and the test solution (Table 10).
<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Molecular Weight (manufacturer)</th>
<th>Weight-Average Molecular Weight Mw</th>
<th>Number Average Molecular Weight Mn</th>
<th>Polydispersivity Ratio P</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-500</td>
<td>413,000</td>
<td>1,097,367</td>
<td>9.11 E-7</td>
<td>1 E+12</td>
</tr>
<tr>
<td>T-70</td>
<td>69,700</td>
<td>96,917</td>
<td>1.03 E-5</td>
<td>9 E+9</td>
</tr>
<tr>
<td>T-40</td>
<td>35,500</td>
<td>58,042</td>
<td>1.72 E-5</td>
<td>3 E+9</td>
</tr>
<tr>
<td>T-10</td>
<td>10,000</td>
<td>14,143</td>
<td>7.07 E-5</td>
<td>2 E+8</td>
</tr>
<tr>
<td>Test solution</td>
<td>-</td>
<td>380,562</td>
<td>2.63 E-6</td>
<td>1 E+11</td>
</tr>
</tbody>
</table>

Table 10. Molecular weight distribution statistics for the dextran fractions and the test solution.

**T-500**

![Elution curve for dextran fraction T-500](image)

Figure 59. Elution curve for dextran fraction T-500.
Figure 60. Elution curve for dextran fraction T-70.

Figure 61. Elution curve for dextran fraction T-40.
Figure 62. Elution curve for dextran fraction T-10.

Figure 63. Elution curve for the test solution.
All dextran fractions have high polydispersivity, which allows for the preparation of a test solution that covers a wide range of molecular sizes. The width of the molecular weight distribution of the test solution is directly related to the applicability range of the method. Molecular weights can be converted to molecular sizes by Equation 16 (Worch, 1993). The relationship is plotted in Figure 64 for molecular weights between 1,000 and 1,000,000. It includes molecule sizes from 2 nm to 65 nm. Figure 65 presents a more detailed view at the sizes measured by nitrogen adsorption. The average pore sizes determined for sintering temperatures between 550°C and 1000°C (6.5 nm - 10.5 nm) equal those of dextran molecules with weights between 13,300 g/mole and 35,500 g/mole. It is important to note that even though at 1000°C the measured average pore size is that of a 35,500 grams/mole molecules, bigger molecules are expected to pass through the membrane due to the variance of the pore size distribution, which was found to increase significantly as the sintering temperature increases.

Figure 64. Molecular weight-size correlation (Worch, 1993).
Figure 65. Range of pore sizes for the alumoxane derived membranes in the molecular weight-size correlation.

The effect of sintering temperature on the MWCO was investigated. Membranes were fired at 600°C, 1000°C and 1100°C and its cut off measured. Although some samples were found to have dissimilar MWCO, several samples presented the same value, which was taken as the MWCO corresponding to the alumoxane derived membrane. Between 600°C and 1000°C no variation in MWCO was detected, in spite of the fact that the average pore size measured by nitrogen adsorption increases 4 nm. For samples fired at higher temperatures the rejection curve could not be obtained, as the pore size goes beyond the molecular size of the dextrans in the test solution. The MWCO of the samples were all in the order of 40,000 Daltons (Table 11).
<table>
<thead>
<tr>
<th>Sample Nr.</th>
<th>Firing Temperature (°C)</th>
<th>MWCO (Daltons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>600</td>
<td>39,810</td>
</tr>
<tr>
<td>10</td>
<td>600</td>
<td>39,810</td>
</tr>
<tr>
<td>13</td>
<td>1000</td>
<td>39,810</td>
</tr>
<tr>
<td>14</td>
<td>1000</td>
<td>38,019</td>
</tr>
</tbody>
</table>

Table 11. MWCO of acetic acid alumoxane derived membranes.

The MWCO of same samples differed from the overall trend due to several problems: incomplete coating in the fabrication process was one of the most important factors, since a defective or uneven support needs to be carefully treated to achieve a satisfactory coating. Cracks in the active layer membrane can be caused by rapid cooling of the sample. An imperfect sealing between the ceramic and the plastic ring to which it was attached to fit the filtration cell can also result in erroneous MWCO values. However, this condition is easily detected because the permeate flux is significantly higher than expected. In the remaining cases, imperfections may not be noticed until the experiment is finished and even then are difficult to identify.

Figure 66 is a typical rejection curve for alumoxane derived membranes, showing a log MWCO of 4.6, or 39,810 daltons.
Figure 66. Rejection curve of an acetic acid alumoxane derived membrane fired at 600°C.

**Ferroxanes**

Ferroxanes derived ceramic membranes prepared by Jerome Rose (CEREGE, Aix-en-Provence, France) were characterized by X-ray diffraction, nitrogen adsorption and AFM. MWCO measurements were also performed on ferroxane membranes cast onto supports.

X-ray diffraction analysis showed that the lepidocrocite particles reacted with the acetic acid to yield an amorphous material; after firing to 300°C, the diffraction patterns indicate that the transformation to hematite has occurred.

Nitrogen adsorption/desorption experiments were carried out for lepidocrocite, the starting material in the preparation of ferroxanes, and the reacted lepidocrocite, before and after sintering. The lepidocrocite used in the synthesis of acetic acid ferroxane had a mean diameter of 52.8 nm and a standard deviation of 39.8 nm (Figure 67).
Figure 67. Pore volume distribution of lepidocrocite used in the synthesis of ferroxanes.

An important reduction in pore sizes are observed for the reacted material, both before and after firing. The distribution becomes narrow (Figure 68), which indicates that the lepidocrocite reacts with the acetic acid to yield particles rather uniform in size. The measurements are presented in Table 12.

<table>
<thead>
<tr>
<th>Lepidocrocite + AA</th>
<th>Lepidocrocite +AA fired at 300 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>Mean</td>
</tr>
<tr>
<td>12.68</td>
<td>13.48</td>
</tr>
<tr>
<td>St. dev.</td>
<td>St. dev.</td>
</tr>
<tr>
<td>8.80</td>
<td>8.38</td>
</tr>
</tbody>
</table>

Table 12. Ferroxanes pore size distribution statistics.
AFM scans were obtained for pre-fired and fired ferroxanes (Figures 69 through 72). The surfaces appear to be rougher than the alumoxane's. The features observed are in the order of 200 - 400 nm in size. The fired samples exhibit a similar topography than the pre-fired ones; this result is in accord with the nitrogen adsorption measurements of pore size distribution for both samples.
Figure 69. AFM scan of acetic acid ferroxane.

Figure 70. AFM scan of acetic acid ferroxane.
Figure 71. AFM scan of acetic acid ferroxane fired to 300°C.

Figure 72. AFM scan of acetic acid ferroxane fired to 300°C.
The MWCO determinations showed a rather diffuse cut off (Figure 73). The MWCO was found to be 630,900 daltons.

**REJECTION vs. MW**

![Graph showing rejection vs. MW](image)

Figure 73. Rejection curve of a ferroxane derived membrane.

*Error in MWCO experiments*

There are several possible sources of error in the MWCO determinations. Extreme caution was taken to prepare all the test solutions as exactly as possible. Before each experiment, deionized water was circulated through the tubing in the experimental set up for half an hour. During the filtration, the feed flow and pressure inside the cell was continuously monitored, as well as the permeate flux. However, small variations in those conditions may have occurred and the short periods of time required for the system to return to the normal
operation conditions may have an influence in the separation performance of the membrane. These errors are operator related and difficult to quantify in terms of percentage.

Errors in the GPC analysis have two possible causes: poor calibration and inaccuracy in the fraction collector. The calibration curve can be improved using a refractive index detector within the GPC system. In the absence of the detector, the calibration curve had to be built with concentration data from fractions collected every milliliter during a run with each dextran fraction. It was not possible to collect smaller volumes, because the concentrations in the samples were too low and fell in the order of magnitude of the background organic carbon content. One of the consequences of this fraction collection is that the value obtained is an average of the real concentration of the eluate during the collection time. Each sample had to be diluted with ultrapure water to run TOC analysis. The TOC analyzer has a maximum coefficient of variation (CV) of 2% in the measurements. With respect of the fraction collector, it was programmed to sample every milliliter, but the last and the first drop were often lost due to the movement of the arm in the instrument. This inaccuracy in the measurement of the volume collected can be estimated knowing the volume of each drop and assuming that the maximum error in each sample a default or an excess of two drops (the first and the last).

All the above also applies to errors in measuring the samples. Assuming that the error due to the filtration stage can be minimized, we can calculate the total inaccuracy of the MWCO determination from the error in the instruments used.

The flow rate of the eluate in the GPC can be expressed in terms of drops per minute. A rate of 1 ml/min. can be translate in this case as 30 drops/min. Then the error in the volume determination of the fractions is $1 \pm 0.067 \text{ ml}$. Each sample was diluted to 3 ml, so $V_{\text{final}} = 3 \times V_{\text{initial}}$. The following statistic equation can be applied to calculate the resulting error:

$$SD(a \times x) = a \times SD(x)$$

(28)
where SD is the standard deviation and a is a constant. The volume of each fraction is then $3 \pm 0.2$ ml, and the CV is 6.7%.

The concentration (mass/volume) was measured. Values with an error higher than 2% were discarded. Taking that CV as representative for all the analysis, we can assume that it is associated with the measurements of the mass. Equation 29 gives the relationship between the CV of two values and its quotient.

$$CV(x/y) = \sqrt{CV(x)^2 + CV(y)^2}$$  \hfill (29)

The concentration values have a CV of 6.96%. Finally the error in the rejection will be the error of the ratio of concentrations, since adding a constant does not introduce additional inaccuracy. Both permeate and feed concentration were determined with the same CV; so, the percentage error for the rejection is 9.8%.

The MWCO for the alumoxane derived membranes is $39,362 \pm 3,857$ daltons; for ferroxane derived membranes $630,900 \pm 61,828$ daltons.
Chapter 5

Summary and Conclusions

Three filters were evaluated as support materials for alumoxane membranes. Anodiscs (Whatman) did not have the necessary thermal resistance and were discarded. The alumina supports from Refracton Tech., Inc. proved to be effective as supports for alumoxane derived ceramic membranes. The alumina filters prepared in our laboratory are promising support materials and have the possibility of being fabricated in different shapes and thickness as required, without depending on a supplier.

The MWCO of the alumoxane derived ceramic membranes was found to be in the order of 40,000 daltons, which falls in the range of ultrafiltration. Alumoxane particles can be deposited on a support to form an asymmetric membrane, but an incomplete coverage of the support surface was often observed. When a second coating was applied, after sintering the first, the permeability of the membranes was so low that even it was not possible to perform MWCO measurements. Thus, it is essential to ensure the complete coating the first time. The same effect of decreased permeability was observed if a membrane was fired twice at temperatures above 800°C.
The sintering temperature did not show to have any significant effect on the MWCO of the membrane between 600°C and 1000°C. This can be due in part to the almost negligible change in pore size, if the whole distribution is considered, and also in the error associated with the MWCO experimental set-up in this work. Formation of α-alumina was observed at sintering temperatures above 1000°C. The transformation to this phase is desirable, as it confers higher resistance to extreme pH to the membrane. The pore size of the α-alumina membrane was found to be much larger and the MWCO fell out of the measuring range of the experimental set up in this work. From the nitrogen adsorption data, we observed that the pore size distribution becomes too wide and it falls out of the ultrafiltration range and thus, the MWCO value is of no practical interest for this work.

In her work, Bailey (1998) concludes that the use of different ligand precursors (i.e., acetic acid, methylethylacetic acid) does not produce membranes with greatly different pore sizes and suggests the possibility of better control through firing conditions. We did not identify in this work any improvement in the pore size control capabilities of sintering temperature and time with respect to the use of different precursors. Average pore sizes of 10.7 nm and 15.0 nm were reported for acetic acid alumoxanes and methylethylacetic acid respectively. The change in the average pore size of acetic acid alumoxane achieved by the variation of sintering temperatures was found to be in the same order of magnitude: 6.48 nm at 550°C and 10.47 nm at 1000°C.

Ferroxanes are viable precursors for porous ceramic membranes. The pore sizes obtained are larger than those obtained from alumoxane derived membranes. However, the sintering temperature, and thus the energy requirements for producing these membranes, is significantly lower.
Chapter 6

Further Research

Several research questions are posed as a result of this work.

The MWCO of alumoxane derived membrane was investigated, but other parameters that describe membrane performance are also of interest. Fouling of the alumoxane membranes needs to be estimated. Cross flow filtration experiments can give a more correct assessment on how the membrane will perform.

Ferroxanes proved to be viable precursors to ceramic membranes, but much characterization work is still needed. Fouling and cross flow filtration experiments need also to be carried out, as in the case of alumoxane membranes.

In both cases, the achievement of smaller particles in the cleavage reaction of the mineral with the carboxylic acid will open the possibility of ceramic membranes with pore sizes in the order of angstroms, such as needed for gas separations and fuel cells.

Finally, the environmental benign character of this material needs to be proved by a life cycle assessment, that compares the new product to organic membranes and ceramic membranes manufactured by the sol-gel process for each specific application.
References


